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Inspection Manual for Enforcement of New Source Performance Standards Phosphate Fertilizer Plants

Research Corp of New England, Wethersfield, Conn

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INSPECTION MANUAL FOR ENFORCEMENT OF NEW SOURCE PERFORMANCE STANDARDS

PHOSPHATE FERTILIZER PLANTS

U.S. ENVIRONMENTAL PROTECTION AGENCY
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16 ABSTRACT

The document presents guidelines to enable enforcement personnel to determine whether new or modified phosphate fertilizer production facilities comply with New Source Enforcement Standards. Key parameters identified during the performance test are used as a comparative base during subsequent inspections to determine the facility's compliance status. The several regulated processes, their atmospheric emissions and emissions controls are described. Inspection methods and types of records to be kept are discussed in detail.

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PHOSPHATE FERTILIZER PLANTS

By

Contract No. 68-01-3173

Prepared For

U.S. Environmental Protection Agency
Division of Stationary Source Enforcement
Washington, D.C.

March 1977

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SECTION 1

INTRODUCTION

In accordance with Section 111 of the Clean Air Act (42 USC 1857, et seq.), the Administrator of the U.S. Environmental Protection Agency (EPA) promulgated emission standards with an effective date of August 4, 1975 for the phosphate fertilizer industry. These new Source Performance Standards (NSPS) limit fluoride emissions from the following phosphate fertilizer processes:

1. Wet Process Phosphoric Acid Plants
2. Super Phosphoric Acid Plants
3. Diammonium Phosphate Plants
4. Triple Superphosphate Plants
5. Granular Triple Superphosphate Storage Facilities

EPA has issued a final guideline document for control of fluoride emissions from existing phosphate fertilizer plants.

Applicable laws permit EPA to delegate implementation and enforcement authority to the states or local regulatory agencies. Such enforcement requires inspection of facilities that must comply with NSPS. The purpose of this inspection is:

1. To determine that the facilities with their control equipment comply with the regulations.

2. To ensure that facilities are operated and maintained in a manner consistent with good air pollution control practices.

Phosphate fertilizer plants generally consist of a number of processes, some of which are quite complex, that require air pollution control equipment. In order to make a successful inspection within a reasonable time, it is essential that inspectors are well prepared for inspection visits.

This manual will provide the air pollution inspector with necessary background information to determine at any time whether or not a plant's operating parameters are consistent with operation during performance tests which have indicated compliance of emission sources.

This manual will also assist the inspector in preparing for his inspection visit to phosphate fertilizer plants by providing:

1. Descriptions of the five fertilizer processes covered by NSPS;

2. Discussions of the emission control equipment used by the phosphate fertilizer industry; and

3. Procedures for inspecting the emission control equipment both during and after performance testing.

SECTION 2

PHOSPHATE FERTILIZER INDUSTRY

The phosphate fertilizer industry, a segment of the agricultural chemical industry, produces and markets commodities bearing the basic nutrients--nitrogen, phosphorous, and potash--for crop production. The industry is totally dependent on phosphate rock deposits, which provide all fertilizer phosphorous.

The principal raw material in the deposits is fluorapatite, $Ca_5(PO_4)_3F$, in which the phosphorous is poorly available as a nutrient to most growing plants. As normal superphosphate, however, the phosphorous can be used by plants for growth. Although this product was first made in 1850, it was not until about 1950 that the potential of the phosphate fertilizer manufacturing industry was recognized. Fertilizer products that were of little importance in 1950 were major nutrient suppliers by 1965.

The production of phosphate has been on the increase since 1960, exceeding 5×10^6 tons P_2O_5 in 1971. In that same year, over 1×10^6 tons of triple superphosphate and 2×10^6 tons of ammonium phosphates were produced.

Phosphate fertilizer production begins with the mining of phosphate rock, proceeds with the chemical production of phosphoric acid and its subsequent processing to diammonium phosphate, superphosphoric acid or triple superphosphate, and terminates with fertilizer formulation and blending.

The structure of the phosphate industry is very complex as shown in Figure 2-1. This schematic illustrates the interrelationship of the various products manufactured by the industry. Many plants consist of more than one phosphate fertilizer production process and include non-phosphate operations such as ammonia and sulfuric acid production.

The basic chemical producers of phosphate fertilizers are generally not identifiable as single product firms, for most fertilizer production is conducted as a subsidiary activity in well-diversified corporations such as chemical manufacturers or petrochemical companies. Some companies are farm cooperatives while others derive the main portion of their revenue from totally unrelated activities. Generally, the basic chemical producers own the source of their raw materials, the phosphate rock mines.

Figure 2-1: Organization of the Phosphate Fertilizer Industrial Processes

Because the major phosphate rock mining area of the United States is in Florida, much of the U.S. phosphate industry is located in this state. One major product, triple superphosphate, is shipped to the Midwest and other areas for bulk blending or for the production of homogenous fertilizers by ammoniation of superphosphate. Other important sources of phosphate rock are located in Tennessee, North Carolina, and the Rocky Mountain area (Idaho and surrounding states).

Normal superphosphate is usually produced near the consumption point rather than near the phosphate ore. Most of these plants are in the Southeast and on the East Coast where the fertilizer industry first developed in the United States.

SECTION 3

SUMMARY OF NEW SOURCE PERFORMANCE STANDARDS (NSPS) AND REGULATIONS

Standards of air pollution control performance for five affected facilities within the phosphate fertilizer industry were proposed on October 22, 1974 (39 FR 37502). The final version of the standards was published on August 6, 1975 (40 FR 33152) with an effective date of August 4, 1975. These standards are promulgated under the authority of Section 111 (a), (b), and (c) of the Clean Air Act, and apply to NEW SOURCES for which construction or modification commenced after the publication of proposed regulations; i.e., October 22, 1974. These standards are concerned only with fluoride emissions within the affected facilities.

Section 111(d) of the Clean Air Act requires that EPA establish procedures under which states must develop emission standards for certain pollutants from existing sources for which NSPS have been promulgated. To accomplish this, EPA proposed on October 7, 1974 a procedure for control of "designated pollutants" from "designated facilities" and promulgated that procedure on November 17, 1975 (40 FR 53340). Designated pollutants are pollutants which are not included on the lists published under Section 108(a) (National Ambient Air Quality Standards) or Section 102 (b)(1)(A) (Hazardous Air Pollutants) of the Clean Air Act, but for which NSPS have been established under Section 111(b). A designated facility is an existing facility which emits a designated pollutant and for which NSPS have been promulgated.

As required by the procedure, EPA first defined designated pollutants, such as fluoride, as either a welfare-related or a health-related pollutant, and then established a guideline for existing sources which recommends a level of emission control for these sources. This guideline, which has determined fluoride emissions from phosphate fertilizer plants to be a welfare-related pollutant, was published in April 1976 and was announced to the public for comment on May 12, 1976 (41 FR 19585). The final guideline was published in November 1976 and announced to the public on March 1, 1977 (42 FR 12021). This has been incorporated in the State's implementation plan.

This section will describe the NSPS for the phosphate fertilizer industry, the emission standards recommended by the guideline for existing sources, and also the state regulations related to fluoride emissions now existing.

4.1 Federal Emission Standards

NSPS limit total fluoride emissions to the atmosphere from phosphate fertilizer plants and permit different emission rates for each of the five major components of the industry category. These allowed fluoride emission rates are listed below:

a. Wet Process Phosphoric Acid (WPPA) plants:

   No more than 10 grams of total fluoride per metric ton of P_2O_5 input to the process (0.020 lb/ton).

b. Superphosphoric Acid (SPA) plants:

   No more than 5.0 grams of total fluoride per metric ton of P_2O_5 input to the process (0.010 lb/ton).

c. Diammonium Phosphate (DAP) plants:

   No more than 30 grams of total fluoride per metric ton of P_2O_5 input to the process (0.060 lb/ton).

d. Triple Superphosphate (TSP) plants, including both Granular Triple Superphosphate GTSP) and Run-Off Pile (ROP) TSP process and ROP-TSP storage facilities:

   No more than 100 grams of total fluorides per metric ton of P_2O_5 input to the process (0.20 lb/ton).

e. Granular Triple Superphosphate (GTSP) storage facilities:

   No more than 0.25 grams of total fluoride per hour per metric ton of P_2O_5 stored (5.0×10^{-4} lb/hr/ton stored).

Standards for visible emissions for DAP plants, TSP plants and GTSP storage facilities were proposed, but were later deleted because there was no direct correlation between fluoride emissions and plume opacity.

The final guideline document recommends that the fluoride emissions for existing phosphate fertilizer facilities be as follows:

a. 0.01 g/kg P_2O_5 for WPPA production (0.02 lb/ton).

b. 0.005 g/kg P_2O_5 for SPA production (0.01 lb/ton).

c. 0.030 g/kg P_2O_5 for DAP production (0.05 lb/ton).

d. 0.100 g/kg P_2O_5 for ROP-TSP production and storage (0.2 lb/ton)

e. 0.100 g/kg P_2O_5 for GTSP production (0.2 lb/ton).

f. 2.5×10^{-5} g/hr-kg P_2O_5 for GTSP storage (5.0×10^{-5} lb/hr/ton).

3.1.1 Monitoring and Reporting

As required by the NSPS, the owner or operator of any WPPA, SPA, GAP or TSP plant shall install, calibrate, maintain and operate monitoring devices which can be used to determine

1. the mass flow rate of phosphorous-bearing feed material to the process, and

2. the total pressure drop across the process scrubbing system.

These devices shall have an accuracy of ±5 percent over their operating range.

The owner or operator of these plants also shall maintain a daily record of equivalent P_2O_5 feed by using

1. the mass flow rate of phosphorous-bearing feed material and

2. the percent P_2O_5 content measured by the molybdovanadophosphate spectrophotometric method (Method 9 as described in the 11th edition of Official Methods of Analysis of Association of Official Agricultural Chemists [AOAC]).

The owner and operator of any GTSP storage facility shall maintain

1. an accurate account of TSP in storage to permit the determination of the amount of equivalent P_2O_5 stored, and

2. a monitoring device which measures and records the total pressure drop across the process scrubbing system. This monitoring device shall have an accuracy of ±5 percent over its operating range.

3.1.2 Performance Testing

The NSPS require that the owner or operator of a source subject to the performance standards conduct a test under representative operating

conditions within 60 days after achieving maximum production rate but not later than 180 days after initial startup, and that he furnish a written report of the results of the test to the Environment Protection Agency, Office of General Enforcement (40 CFR 60.8). Furthermore, the owner or operator of an affected facility should provide the Administrator 10 days prior notice of the performance test.

Reference methods in Appendix A of Part 60 of Chapter I, Title 40 CFR (36 FR 24876, 41 FR 23060) shall be used to determine compliance with the standard as follows:

1. Method 13A or 13B for the concentration of total fluorides and the associated moisture content,

2. Method 1 for sample and velocity traverses,

3. Method 2 for velocity and volumetric flow rate, and

4. Method 3 for gas analysis.

3.1.3 Applicability of Standards

The NSPS classify and define the affected facilities as the following:

1. Wet-Process Phosphoric Acid (WPPA) plant:

   Any facility manufacturing phosphoric acid by reacting phosphate rock and acid. This includes any combination of reactors, filters, evaporators, and hot wells.

2. Superphosphoric Acid (SPA) plant:

   Any facility which concentrates wet-process phosphoric acid to 66 percent or greater P_2O_5 content by weight for eventual consumption as a fertilizer. This includes any combination of evaporators, hot wells, acid sumps and cooling tanks.

3. Granular Diammonium Phosphate (DAP) plant:

   Any plant manufacturing granular diammonium phosphate by reacting phosphoric acid with ammonia. This includes any combination of reactors, granulators, dryers, coolers, screens and mills.

4. Triple Superphosphate (TSP) plant:

   Any facility manufacturing triple superphosphate by reacting phosphate rock with phosphoric acid. This

includes any combination of mixers, curing belts (dens), reactors, granulator dryers, cookers, screens, mills and any facilities which store run-of-pile TSP.

5. Granular Triple Superphosphate (GTSP) Storage Facilities:

   Any facility curing or storing granular triple superphosphate. This includes any combination of storage or curing piles, conveyors, elevators, screens and mills.

While phosphate rock mining, rock crushing, sulfuric acid plants and nitric acid plants are commonly an intergral part of the phosphate fertilizer industry, they are subject to separate NSPS and therefore are outside the scope of this manual.

3.2 State Regulations

States in which the majority of phosphate fertilizer plants are located have been applying existing regulations to control fluoride emissions. Selected state regulations are summarized in Table 3-1.

In addition, since each state may have standards for emissions other than fluorides, the inspector is therefore inspecting not only for fluoride violations but also for violations of other state regulations. Therefore, the details of state emission standards and testing regulations must be examined before inspection occurs. The major state standards applicable to phosphate fertilizer plants are those for visible emissions, particulate emissions, and ambient air fluoride concentrations.

TABLE 3-1

SUMMARY OF FLUORIDE AND OTHER EMISSION STANDARDS
RELATED TO PHOSPHATE FERTILIZER PLANTS
IN SELECTED STATES

Location	Fluorides	Particulates	Visible "Ringelmann Coefficient"	Ambient Fluorides Standard
California	2.5 mg/DSCF	"	"	"
Florida	Standards vary with specific process	(1)	2	"
Idaho	"	"	2	"
Iowa	0.4 lb/ton P_2O_5 input max. 100 lb/day	(1)	"	"
Mississippi	0.4 lb/ton P_2O_5	(1)	"	"
Montana	0.3 lb/ton P_2O_5 input	(1)	2	1 ppb (24 hr)
N. Carolina	"	(1) and controlled as chemical fertilizer manufacturing plants	"	"
Texas	"	max. 0.07 grains/ SCF		3.5 ppb (24 hr)
Virginia	"	(1) and controlled as chemical fertilizer manufacturing plants	"	"
Washington	"	"	"	4.5 ppb (1 hr) 3.5 ppb (24 hr) 2.0 ppb (1 wk) 1.0 ppb (1 mo)

NOTES

(1)Rate of emission shall be calculated based on process weights

(2)Visible "Ringelmann Coefficient" 2 is equivalent to 40 percent opacity.

SECTION 4

EMISSION CONTROL EQUIPMENT

Fluorine compounds are the only air [illegible]ants regulated by NSPS for phosphate fertilizer plants. Of the type [illegible]r pollution control equipment available, only those involving adsorption or absorption are capable of removing gaseous fluorine compounds from air. Although solid packed beds of limestone or alumina have been proposed for the removal of fluorine by adsorption, wet scrubbers have been used almost exclusively for control of fluoride emissions.

Most often, the fluoride emissions are controlled by complex scrubbing systems rather than by a single control device. Such systems usually consist of cyclones as primary collectors and a combination of venturi-spray scrubbers as secondary collectors. The emissions from such control devices are then frequently combined into a tall gas scrubber as a final stage. Baghouses and electrostatic precipitators are also used as components in these systems. Figure 4-1 shows a schematic of a typical fluoride scrubbing system; Figure 4-2 is a photograph of the scrubbing system used by one GTSP plant.

Wet scrubbers are air pollution control devices which remove gases and particulates from the stream through scrubbing by liquid. The collection principle is to first bring aerosols and gas molecules close to the collecting bodies (liquid droplets) and then to accomplish the actual collection through a number of short-range physical and chemical mechanisms. The physical and chemical phenomena by which contaminants are removed from the gas stream are called unit mechanisms.

The basic unit mechanism for removal of gases is mass transfer (diffusion), while the driving force for this operation is concentration gradient. The basic unit mechanisms for removal of particulate are the physical forces of interception, inertial impaction, Brownian motion, and particle growth condensation. Wet scrubbing systems exploit both mechanisms to remove particulate and gaseous components from contaminated gas streams.

The knowledge of fluorine compounds present in the gas and scrubbing liquids is of prime importance since each compound has its own adsorption rate and may exist in a gaseous stage and/or as particulate or fume. Consequently, it is very difficult to predict the efficiency of an abatement system.

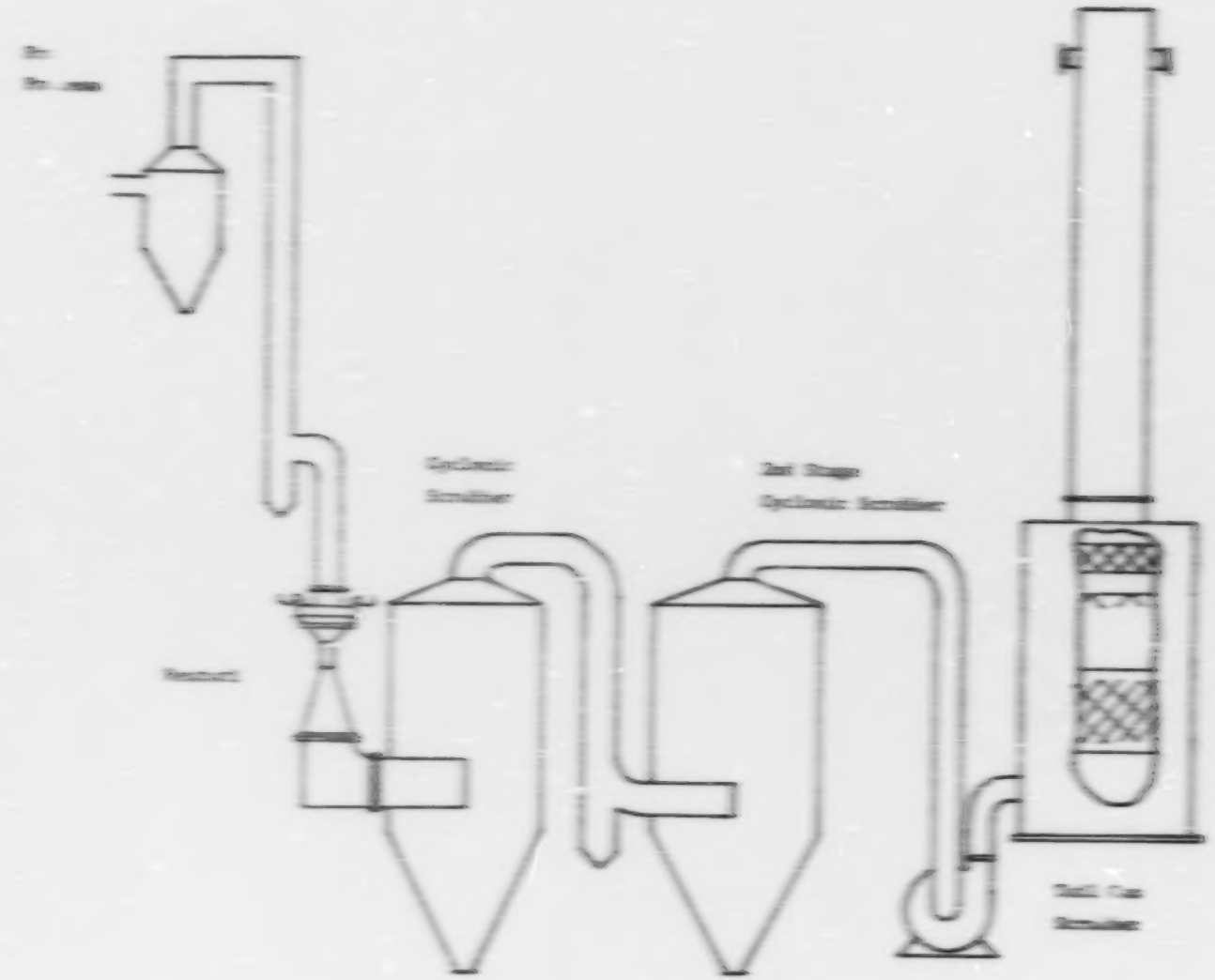


Figure 4-1: Fluorite Scrubbing System

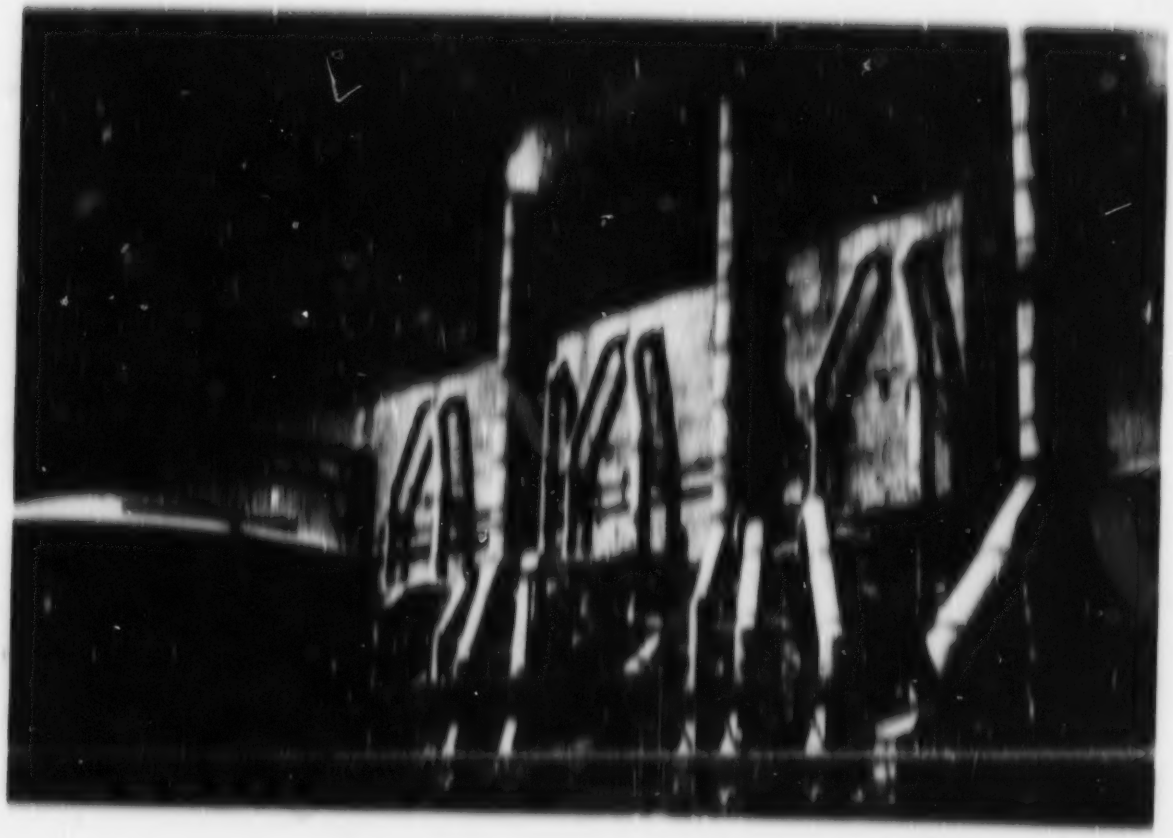


Figure 4-2: Fluoride Control System on GTSP Plant

In general, the extent of the fluorine abatement system required is determined by the following parameters:

1. Inlet fluorine concentration,
2. Allowable fluorine emissions,
3. Outlet or saturated gas temperature,
4. Composition and temperature of the scrubbing liquid,
5. Scrubber effectiveness and number of transfer units,
6. Fluorine compounds present, and
7. Effectiveness of entrainment separation.

The inlet concentration and allowable outlet fluorine emissions must first be established to determine the overall scrubbing requirement. Figure 4-3 shows the relationship between saturated gas temperatures and the overall removal efficiency of the scrubbing device.[1] The gas stream leaving the scrubber is saturated with water vapor. When the scrubber is operated at a relatively low saturated temperature (gas temperature close to the gypsum pond water temperature), the efficiency is high. Since absorption decreases with temperature increase, efficiency is lower at a higher saturated temperature. An additional advantage of scrubber operation at low temperatures is that silica is kept in a gelatinous stage which is easily washed from the scrubbing device. At higher temperature, the silica is crystallized on the scrubber and removed with great difficulty.

The scrubber effectiveness, or the number of transfer units, will determine the overall scrubbing requirements. Figure 4-3 shows the fluorine removal transfer unit formula.

Transfer units are defined by the following formula:

$$NTU = \ln \frac{\text{Inlet } F}{\text{Outlet } F + a}$$

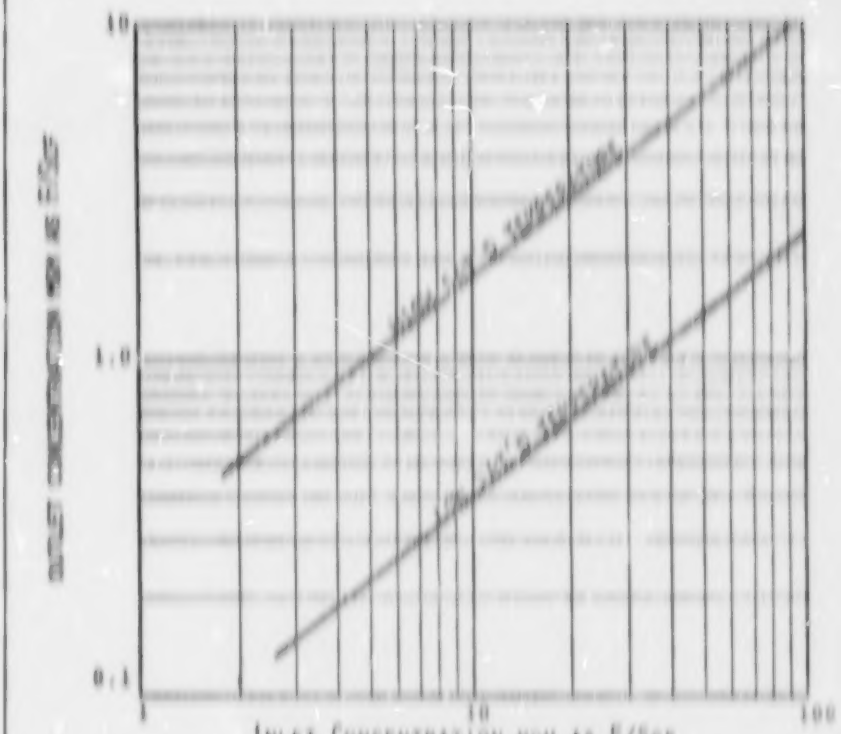
where: a = vapor pressure contribution of fluorine from scrubbing media

Once the overall transfer unit requirements are determined, the number of scrubbing stages may then be set based upon the ability of each scrubbing device employed.

The scrubbers which are likely to perform well in phosphate fertilizer plants include spray towers, venturi scrubbers, cross-flow packed scrubbers, and impingement scrubbers.

4.1 Spray Towers

Spray towers provide the contact necessary for gas absorption by dispersing the scrubbing liquid in the gas phase in the form of a fine



INLET CONCENTRATION HCN AS F/Scf

FLUORINE SCRUBBING

WITH

LOW FLUORINE CONTENT LIQUOR

FLUORINE REMOVAL TRANSFER UNIT FORMULA

$$Nt = \ln \frac{Y_1 - Y_a}{Y_2 - Y_a}$$

N_t = Number of transfer units

Y = Concentration of fluoride in gas

1 = at inlet

2 = at outlet

a = content based upon gas phase equilibrium with concentration of fluoride in scrubbing liquor in concentrations below 5,000 ppm as F this effect is neglected.

Figure 4-3: Relationship Between Gas Temperature and Scrubber Removal Efficiency (Reprint with Permission of the McIlvaine Company from McIlvaine Scrubber Manual, 1976, p. 42, 511)

spray. Cyclonic spray towers eliminate excessive entrainment of scrubbing liquid by utilizing centrifugal force to remove entrained droplets. Figure 4-4 is a schematic of a typical spray tower, while Figure 4-5 shows a cyclonic spray tower being used at a run-of-pile triple superphosphate plant. A tangential inlet is used to impart the spinning motion to the gas stream which flows perpendicular to the water sprays. Pressure drops across the scrubber range from 2-8 inches of water. Although solids handling capacity is high, absorption capacity is limited to about two transfer units.

4.2 Venturi Scrubbers

Although venturi scrubbers are primarily particulate collection devices, they are also successfully applied to gas absorption work and are widely used throughout the phosphate fertilizer industry.

When treating effluent streams requiring a high degree of fluoride removal, venturi scrubbers are often used as the initial component in a multiple scrubber system. Venturi scrubbers can bring about effective contact and gas absorption when sufficient energy is imparted to the gas to atomize the scrubbing liquor and produce very small droplets. The atomization is obtained from velocity differences between the two phases and gas-liquid contact is obtained from turbulence in the venturi throat.

As shown in Figure 4-6, both gas and water-actuated systems are in use, and both types require the use of a mist elimination section for removal of scrubbing liquid. Figure 4-7 shows a photograph of a water-induced venturi in use on a superphosphoric acid plant effluent stream. In this system the scrubbing liquid is introduced at a high velocity through a nozzle located upstream of the venturi throat. The velocity of this water stream is used to pump the effluent gases through the venturi.

Because there is no fan, the water-actuated venturi is mechanically simpler, more reliable, and less costly than the gas-actuated type. In addition, it is relatively insensitive to variations in the gas stream flow rate. Pressure drops of air across these scrubbers are as high as 8 to 20 inches of water, and efficiencies reaching 96 percent have been reported. On the other hand, these units do use large volumes of scrubbing liquid and have high energy requirements for pumping.

A venturi scrubber being used on a DAP process is shown in Figure 4-8.

4.3 Spray-Crossflow Packed Scrubbers

The spray-crossflow packed bed scrubber has been accepted as the most satisfactory fluoride control device available for wet process phosphoric acid plants. As shown in Figure 4-9, the spray-crossflow packed bed scrubber consists of two sections, a spray chamber and a packed bed,

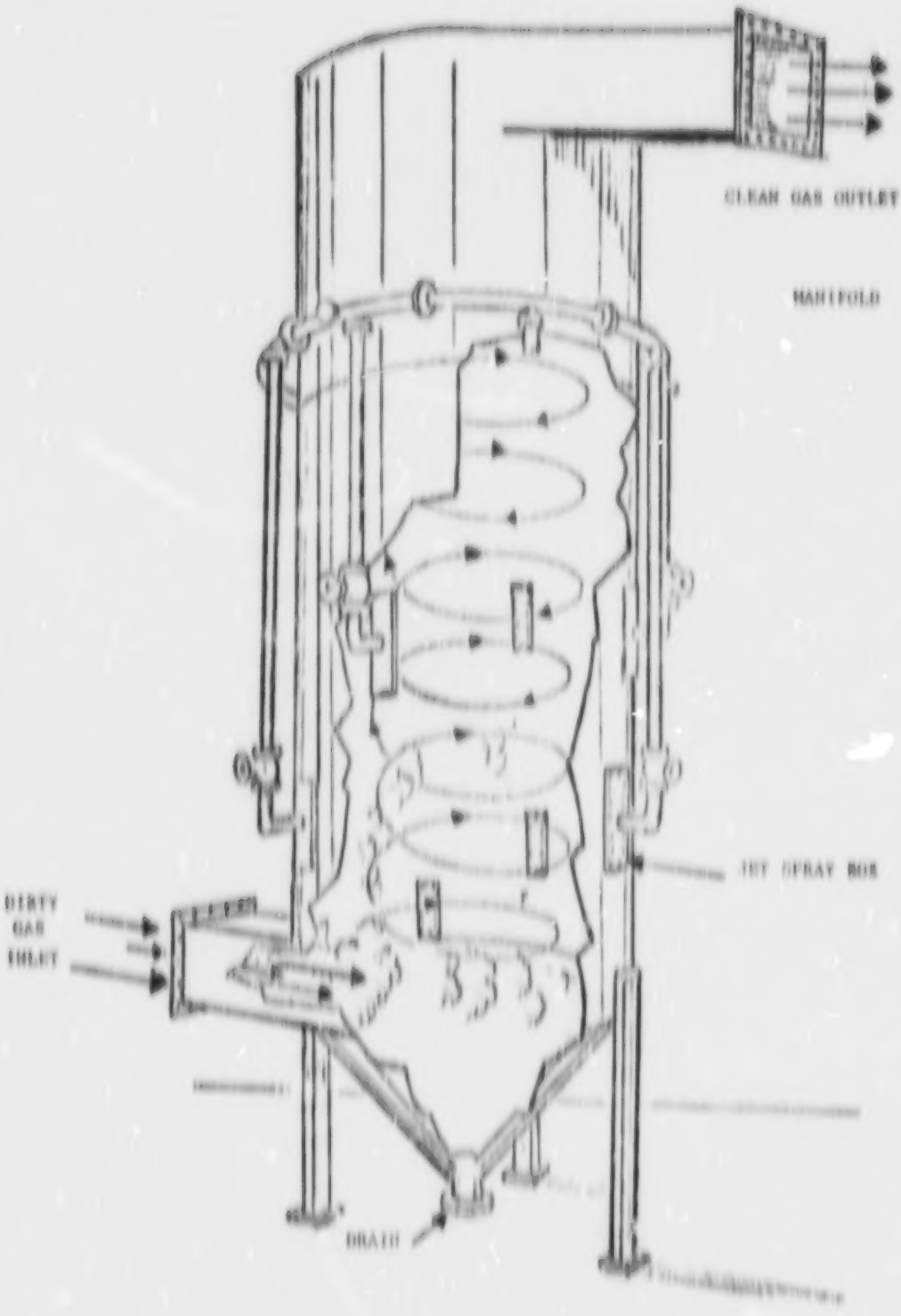


Figure 4-4: Cyclonic Spray Tower Scrubber

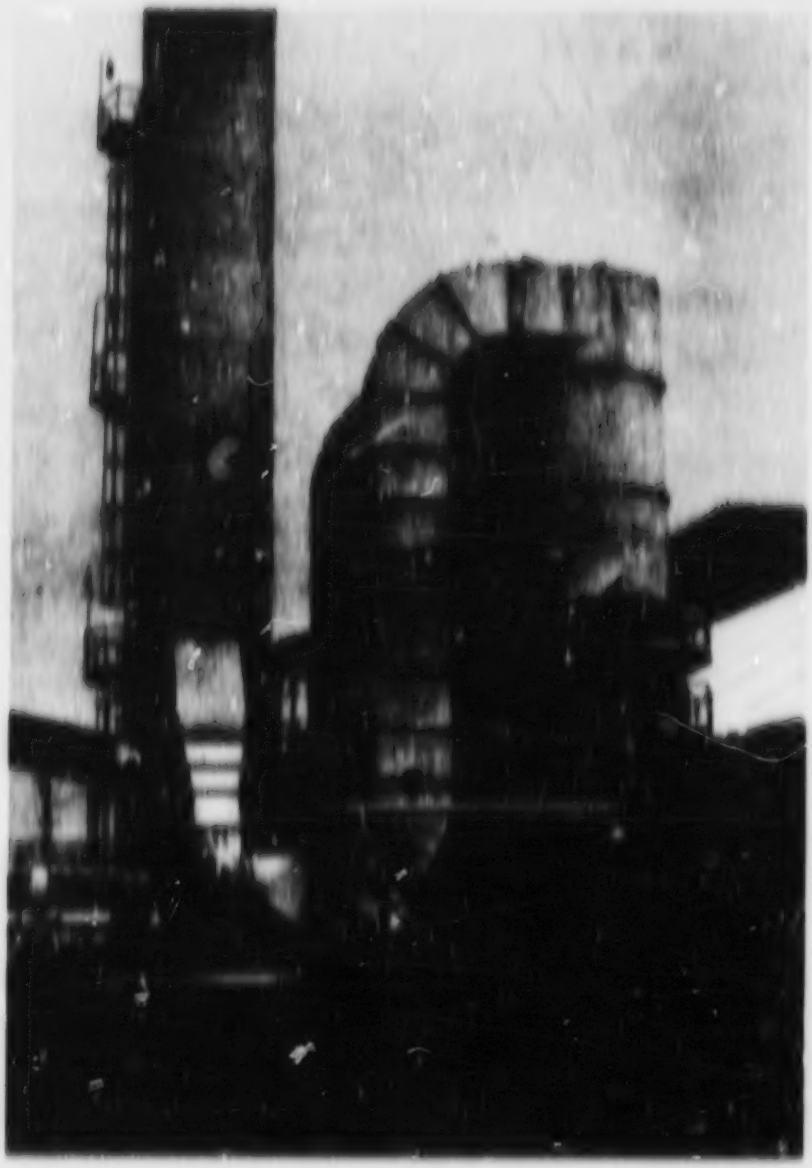


Figure 4-5: Cyclonic Spray Tower on ROP-TSP Plant

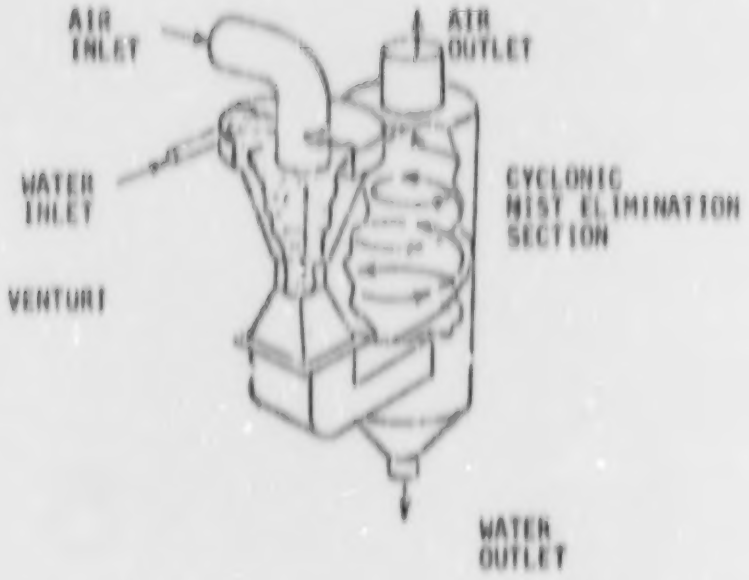


Figure 4-6a: Gas Activated Venturi Scrubber with Cyclonic Mist Eliminator

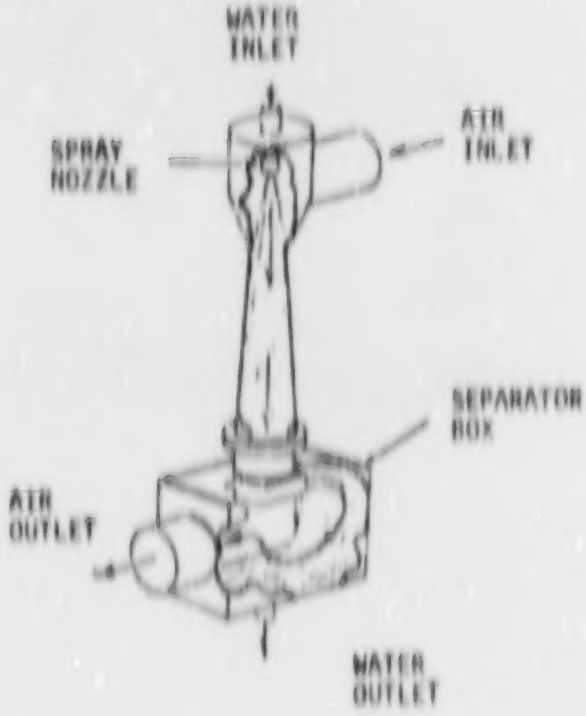


Figure 4-6b: Water Actuated Venturi

Figure A-7: Water-Induced Venturi on SPA Plant

Figure 4-8: Venturi Scrubber on DAP Process Facility

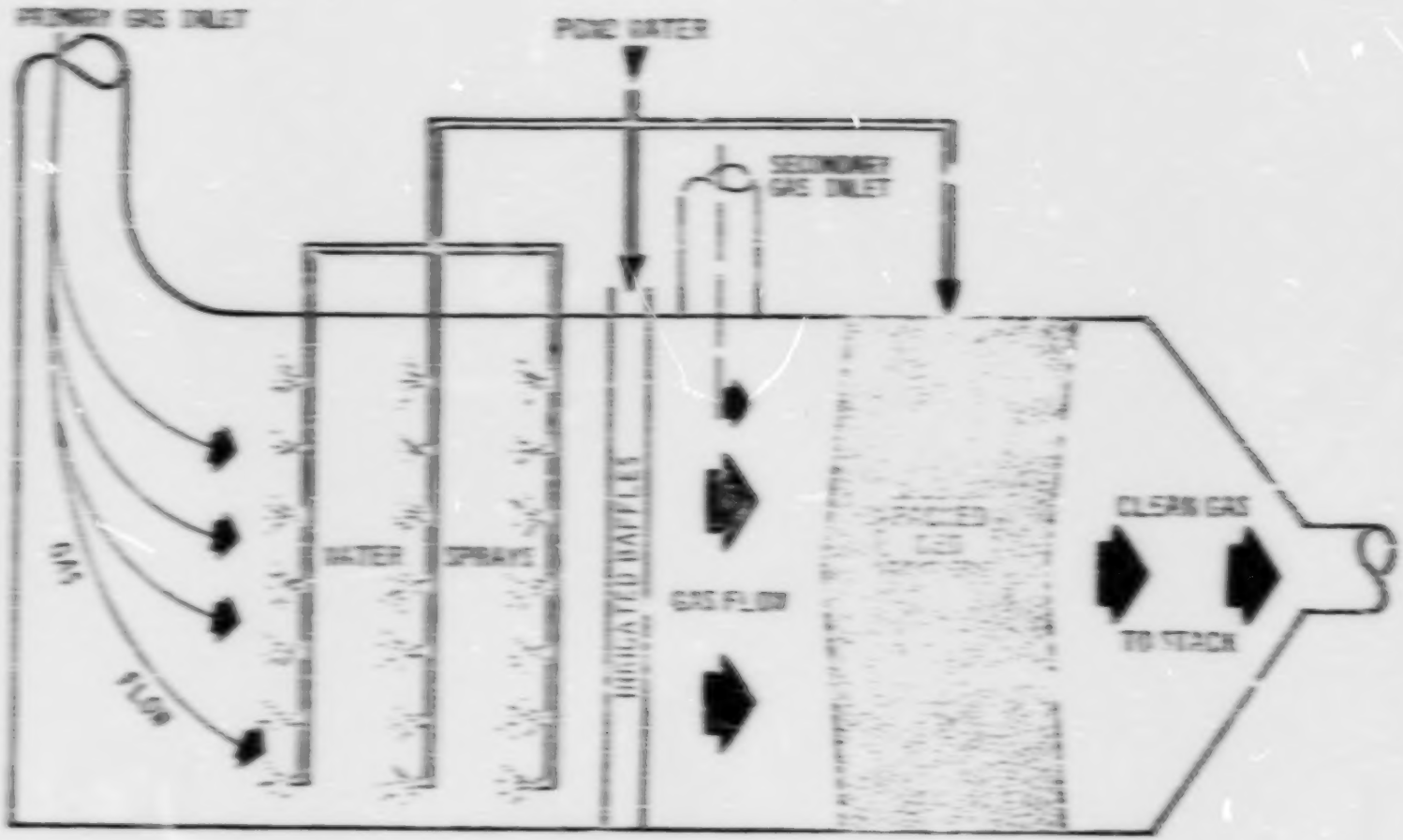


Figure 4-9: Spray Cross-Flow Packed Bed Scrubber

separated by a series of irrigated baffles. Both sections are equipped with gas inlets. Gas streams with high fluoride and particularly high SiF_4 concentrations are treated in the spray chamber before entering the packing. This reduces the danger of plugging in the bed, reduces the loading on the packed stage, and provides some solids handling capacity. The crossflow design operates with the gas stream moving horizontally through the bed with the scrubbing liquid flowing vertically through the packing. Solids deposited near the front of the bed are washed off by a cleaning spray. Pressure losses through the scrubber range from 1-8 inches of water, the average being about five inches.

Recycled gypsum pond water is normally used as the scrubbing liquid in both the spray and packed sections, the ratio of scrubbing liquid to gas ranging from 0.02 to 0.07 gpm/acfm (.045-.156 lpm/m^3/hr) depending on the fluoride content of the gas stream.

Provided that the solids loading of the effluent stream has been reduced enough to prevent plugging, the fluoride removal efficiency of the spray-crossflow packed bed scrubber is limited only by the amount of packing used and the scrubbing liquid. Efficiencies as high as 99.9% have been reported.[2]

Figure 4-10 shows a spray-crossflow scrubber in use at a wet process phosphoric acid plant.

4.4 Impingement Scrubbers

Impingement scrubbers have also been used with success to treat effluent streams containing fluorides. One type of impingement scrubber shown in Figure 4-11 is most effective and is commonly used by the fertilizer industry. This consists of a rectangular chamber with a sloping bottom designed to contain a shallow bath of scrubbing liquor. Gases are driven into the bath at high velocity and water-soluble components are removed by resulting impingement. Water requirements are low (.5-2 gal/$10^3$$ft^3$gas) and efficiencies as high as 99% have been reported.[3] Typically, the pressure drop across the scrubber is 5-15 inches.

4.5 Maintenance of Control Equipment

The maintenance of scrubber systems should be less than that required for fabric filters and precipitation systems if equipment is properly sized and applied. If, however, the scrubber system is improperly designed, maintenance costs can be extremely high.

Preventive maintenance is an important part of any maintenance program, and regular measurement of scrubber efficiency can be used as a tool for preventive maintenance. If the equipment initially functions at designed efficiency, a regular efficiency test of the system can lead

Figure 4-10: Cross-Flow Packed Scrubber on WPPA Plant

Figure 4-11: Self-Induced Spray Type Scrubber (Doyle)
(Reprint with Permission of Pergamon Press from
Industrial Gas Cleaning Equipment, 1966)

to identification and correction of problems long before they are discovered by maintenance personnel.

Some of the problems that can surface on scrubbers in operation include reduction of volumetric flow rate, lowered collection performance, liquid carryover, and scaling. In order to prevent some of these problems from becoming too serious, regular inspections should be carried out. The best indication of scrubber operation is the pressure drop across th unit. Under steady operating conditions, the pressure drop will stay constant within ± 0.2 in. W.G. The scrubber pressure drop should be observed and recorded at least three times a day. Any change of pressure drop might indicate scrubber malfunctioning. An increase in pressure drop will indicate plugging or too high air or scrubbing liquid flow rate. A decreese in pressure drop will indicate a reduction in air or scrubbing liquid flow rate. Scrubber inspections should also include checking of the campers, fan drive belts, spray nozzles, drains, and scrubber feed water clarification system, and scrubber inlet ducts should be examined for leaks or blockage by deposited materials. Any malfunctions should be corrected as soon as possible.

SECTION 5

PHOSPHATE FERTILIZER MANUFACTURING PROCESSES

Five phosphate fertilizer manufacturing processes are regulated by NSPS for the phosphate fertilizer industry. These processes include the manufacture of wet process phosphoric acid and superphosphoric acid and their subsequent processing into diammonium phosphate, run-of-pile triple superphosphate, and granular triple superphosphate. This section of the manual summarizes each of the processes and discusses the sources of fluoride emissions and applicable air pollution control techniques.

5.1 Wet Process Phosphoric Acid (WPPA) Plants

5.1.1 Process Description

Phosphoric acid, a major intermediate in fertilizer technology, is used in the production of superphosphate, ammonium phosphate, and mixed granular fertilizers.

The manufacture of phosphoric acid itself begins with phosphate rock as raw material. Typical phosphate rock from the United States used for wet process phosphoric acid production may contain 31-35% P_2O_5 and 1.5 to 4.0% combined iron and aluminum oxides. The process used for the production of phosphoric acid is often described as the dihydrate process because the gypsum byproduct that is formed is substantially all in the dihydrate form.

Several variations of the dihydrate process are currently in use by the phosphate fertilizer industry. The Dorr-Oliver, St. Gobain, Prayon, and Chemico processes are among the better known schemes. Basically, there is little difference among them, most variations being in reactor design and operating parameters. All process types consist of three major steps: reaction, filtration, and evaporation. A process flow diagram for the production of wet process phosphoric acid is shown in Figure 5-1.

In the first step, ground rock is slurried with acid. Although any common mineral acid may be used to digest phosphate rock, sulfuric acid is normally used on a commercial scale for wet process phosphoric acid manufacture. The use of a 66° Bé acid (93-98% H_2SO_4) is preferred to acids of lower strength.

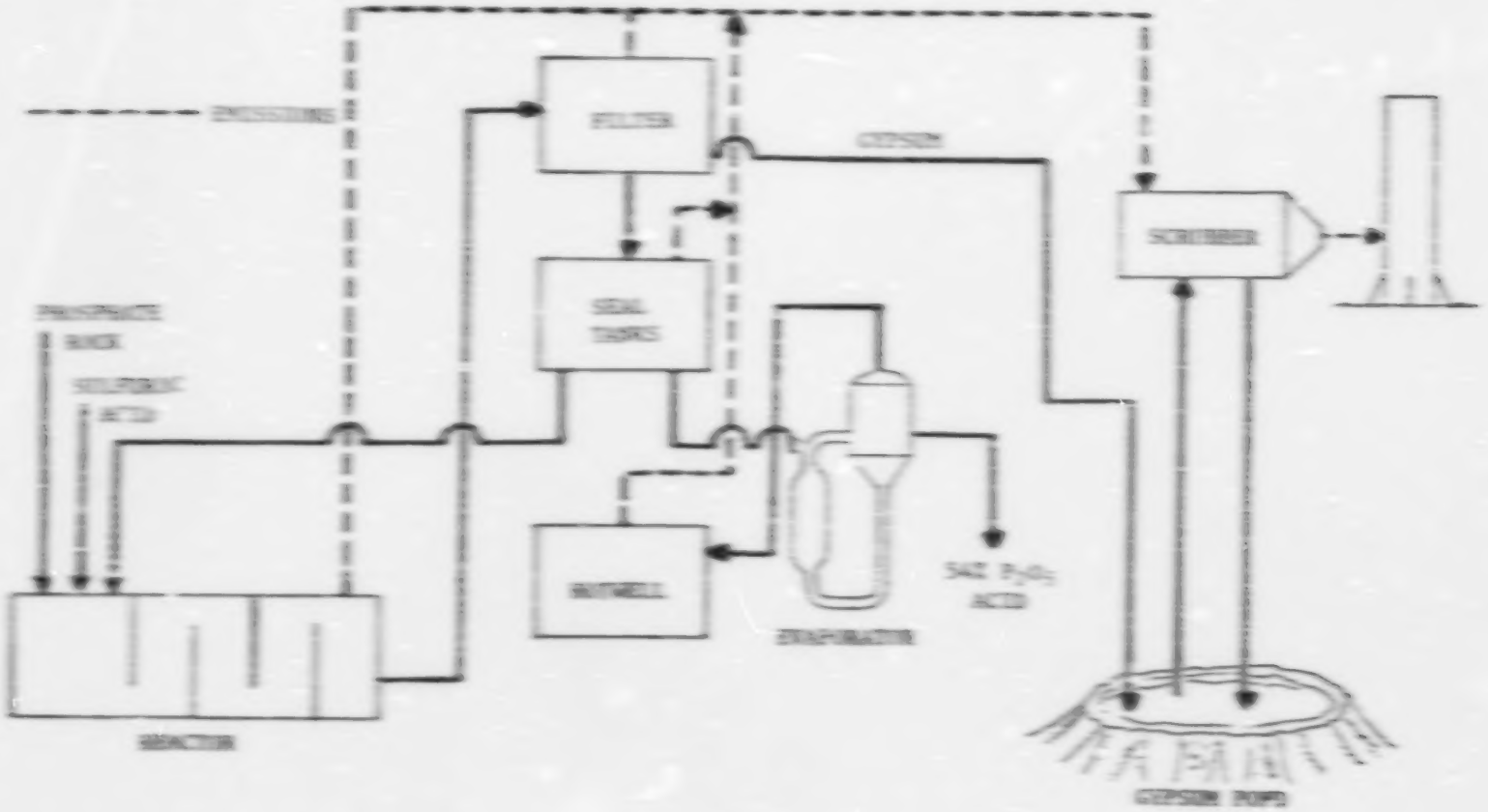


Figure 5-1: Wet-Process Phosphoric Acid Production

The reaction that occurs in this step is described by the net chemical equation:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 3[CaSO_4 \cdot 2H_2O] + 2H_3PO_4 \qquad (5\text{-}1)$$

The tricalcium phosphate in the rock reacts with sulfuric acid and water to yield phosphoric acid and gypsum. This reaction is carried out in the digestion system over a period of approximately eight hours. The reaction itself is completed to a large extent in a matter of minutes, but more time is needed to allow for the proper formation of gypsum crystals. Sulfuric acid and finely-ground phosphate rock are continuously added to a slurry consisting of reactants, products, and enough recycling weak phosphoric acid to maintain fluidity.

Reactions arising from undesirable components in the rock also occur and are a potential considerable source of air pollution. These include the formation of fluorosilicic acid and fluorosilicate which decompose to precipitate in pipelines, filter cloths, and equipment. Under process heat, moisture, and acid conditions, SiF_4 reacts with water to deposit silica as a precipitate in the gas ducts.

The reaction between phosphate rock and sulfuric acid is highly exothermic. Heat is removed from the process by recycling the slurry through a cooler chilled by water vaporization. The slurry is agitated and circulated and a stream of phosphoric acid-calcium sulfate slurry is withdrawn for filtering.

The filtering and washing operations are carried out on a series of filter surfaces. Belt or rotary type horizontal tilting pan filters are superior to other types and are widely used in almost all new plants. After dewatering of the filter cake, the phosphoric acid-rich liquor entrapped within the solid $CaSO_4 \cdot 2H_2O$ crystal matrix is replaced by washing with more and more dilute solutions of phosphoric acid until, on the final wash, recycled make-up water is used for washing. In many plants, the make-up water is recycled from the barometric condenser.

The acid, which is about 30% P_2O_5, is concentrated to about 54% P_2O_5 (industry uses term 54% acid for actual concentrations in 50-58% range) in the third and final step by use of multiple stage vacuum evaporators. These evaporators use steam to distill water overhead and operate under vacuum to maintain low evaporation temperatures. The acid is passed through a series of clarifiers to remove as many trace fines as possible and then it is pumped to storage.

5.1.2 Emission Sources

Air pollutants from wet process phosphoric acid manufacture originate in every step of the process. The digester/reactor is the major source of emissions, accounting for nearly 90% of the fluorides

entering the control system. Additional sources are the filter, the filtrate feed and seal tanks, the flash cooler seal tank, the evaporator system hotwell, and the acid storage tanks. Of course, fluoride emissions will vary depending upon the type of rock treated and the process used. Table 5-1 lists fluoride emission factors for various uncontrolled sources as shown in Figure 5-1.[5]

One plant producing 85,200 lb H_3PO_4 (P_2O_5) per hour has controlled the emissions from these sources to 1.8 lbs of fluoride per day using a wet scrubber. For this particular plant, this represents over 99% control of fluoride emissions.

As stated previously, the source requiring the most attention for control of fluoride emissions is the digester/reactor. Both the reaction vessel itself and the vacuum flash cooler associated with it contribute to the fluoride emissions, the primary source being the reactor tank, where digestion of the phosphate rock releases SiF_4 and HF, as well as some minor constituents.

Reaction heat is removed by cycling part of the reaction slurry through a vacuum flash cooler. Vapors from the cooler are condensed in a barometric condenser and sent to a hotwell while non-condensibles are removed by steam ejection before being vented to the hotwell. Most of the fluorides evolved in the cooler are absorbed by the cooling water in the barometric condenser. Use of air cooling will cause fluoride emissions to be higher.

The filter is the second most important source of fluoride emissions, since most of the fluorides are emitted where the feed acid and wash liquor are introduced to the filter.

The evaporator, which is used to concentrate the product acid from 30 to 54% P_2O_5, is the last significant source of fluoride emissions. Most of the fluorides vaporized during this operation are returned to solution in the system's barometric condensers. The remainder exits with the non-condensibles and is sent through the hotwell which becomes the potential emission source for this operation.

Minor sources of fluoride emissions include vents from sumps, clarifiers, and acid tanks. Collectively, these sources can be significant and may be ducted to a scrubber.

Gaseous fluorides may also evolve from the gypsum pond because of the vapor pressure of the fluoride. The rate of evolution of fluoride will vary with temperature, concentration, absolute pressure, and exposed area of the liquid surface.

In addition to gaseous fluoride emissions, there is likely to be some rock dust generated by the mechanical handling of the rock. This is not likely, however, in a plant using wet rock grinding.

TABLE 5-1

FLUORIDE EMISSION FACTORS

Source	Emission Factor (lb F/ton P_2O_5)
Reactor	.04 - 2.2
Filter	.01 - .06
Miscellaneous (filtrate feed & seal tanks, hot-wells, etc.)	up to .26

5.1.3 Control Equipment and Inspection Procedures

5.1.3.1 Control Equipment

The spray-crossflow packed bed scrubber has been accepted for several years as the most satisfactory fluoride control device available for wet process phosphoric acid plants. Most wet-acid plants built since 1967 have probably installed this scrubber as part of the original design. The conversion of SiF_4 to SiO_2 in the ductwork causes deposits which lead to plugging of air pollution control equipment. Proper maintenance is required to keep equipment functioning efficiently.

Providing that the solids loading of the effluent stream has been reduced sufficiently to prevent plugging, the fluoride removal efficiency of the scrubber is limited only by the amount of packing used and the nature and quantity of the scrubbing liquid. Most well-controlled plants use a spray-packed bed type scrubber to control the combined emissions from the reactor, the filter, and several miscellaneous sources. Efficiencies as high as 99.9% have been reported for WPPA plants.[5]

5.1.3.2 Inspection Procedures

Process Instrumentation

Process information should be collected when the NSPS tests are performed. The inspector should obtain the process rate in terms of the phosphorous-bearing material feed rate and the equivalent P_2O_5 feed rate. The phosphorous-bearing material feed rate should be obtained directly from monitoring instrumentation.

The inspector should check process instrumentation and note the operating parameters being used at the time of inspection. These include the rate of addition of phosphate rock and H_2SO_4 to the reaction system, reaction temperatures, the absolute pressures and temperatures in the evaporator system, and the P_2O_5 content of the product being produced during the test. Finally, all tank levels, liquor flow rates, water temperatures, and power readings should be noted.

Control Device Instrumentation

The inspector should also collect control device data when the NSPS tests are first performed. This may then be used as a reference for future inspections.

Scrubbers

The inspector should make sure all control devices are operative and that the fans are on. He should also note whether fluorine odors

or visible emissions are detectable from the control device. He should read the total pressure drop across the process scrubbing system from a manometer or from gauges on the scrubber instrument panel, check the water flow rate into the scrubber, and make note of any observed leaks or broken seals. Finally, the pH of the scrubbing liquid should be noted.

5.2 Superphosphoric Acid (SPA) Plants

5.2.1 Process Description

Superphosphoric acid, a mixture of polymeric forms of phosphoric acid in addition to orthophosphoric acid, is a dehydration product of 54% P_2O_5 phosphoric acid and is used in the manufacture of high analysis fertilizers and liquid fertilizers. Two commercial processes are used to concentrate the 54% P_2O_5 acid to approximately 70% P_2O_5 acid: submerged combustion and vacuum evaporation.

In the submerged combustion process, dehydration of the acid is accomplished by bubbling hot gases through a pool of the 54% acid in a submerged combustion evaporator. The hot gases, supplied by burning natural gas in a separate chamber, are diluted with air to maintain a gas temperature of 1700°F for introduction into the acid evaporator. As shown in the process schematic in Figure 5-2, clarified 54% P_2O_5 acid is continuously fed to the evaporator from storage, and acid containing concentrated P_2O_5 is withdrawn from the evaporator to product holding tanks. Circulation of water through stainless steel cooling tubes in the product tanks cools the product. The process may be controlled by regulation of the natural gas and air flows to the combustion chamber, the dilution air to the combustion stream, or the amount of acid fed to the evaporator. Water vapor, fluorides, and phosphoric acid mist are driven from the evaporator solution and ducted to control devices.

Vacuum evaporation, the more important commercial method for concentration of phosphoric acid to superphosphoric acid, is shown schematically in Figure 5-3. The procedure for concentrating the acid may vary from plant to plant, the usual source of variation from one process design to another occurring in the method of heating and concentrating the acid. Evaporation may be accomplished by a falling film evaporator or by forced circulation evaporation. Both types of processes require clarified 54% feed acid, and both use high-vacuum concentrators with high-pressure steam to concentrate acid to 70% P_2O_5. In addition, both processes introduce feed acid into a large volume of recycling product acid to maintain a highly concentrated process acid for lower corrosion rates.

In the falling film process illustrated in Figure 5-4, the mixture of concentrated product and feed acid is pumped to the top of the evaporator and distributed to the inside wall of the evaporator tubes.

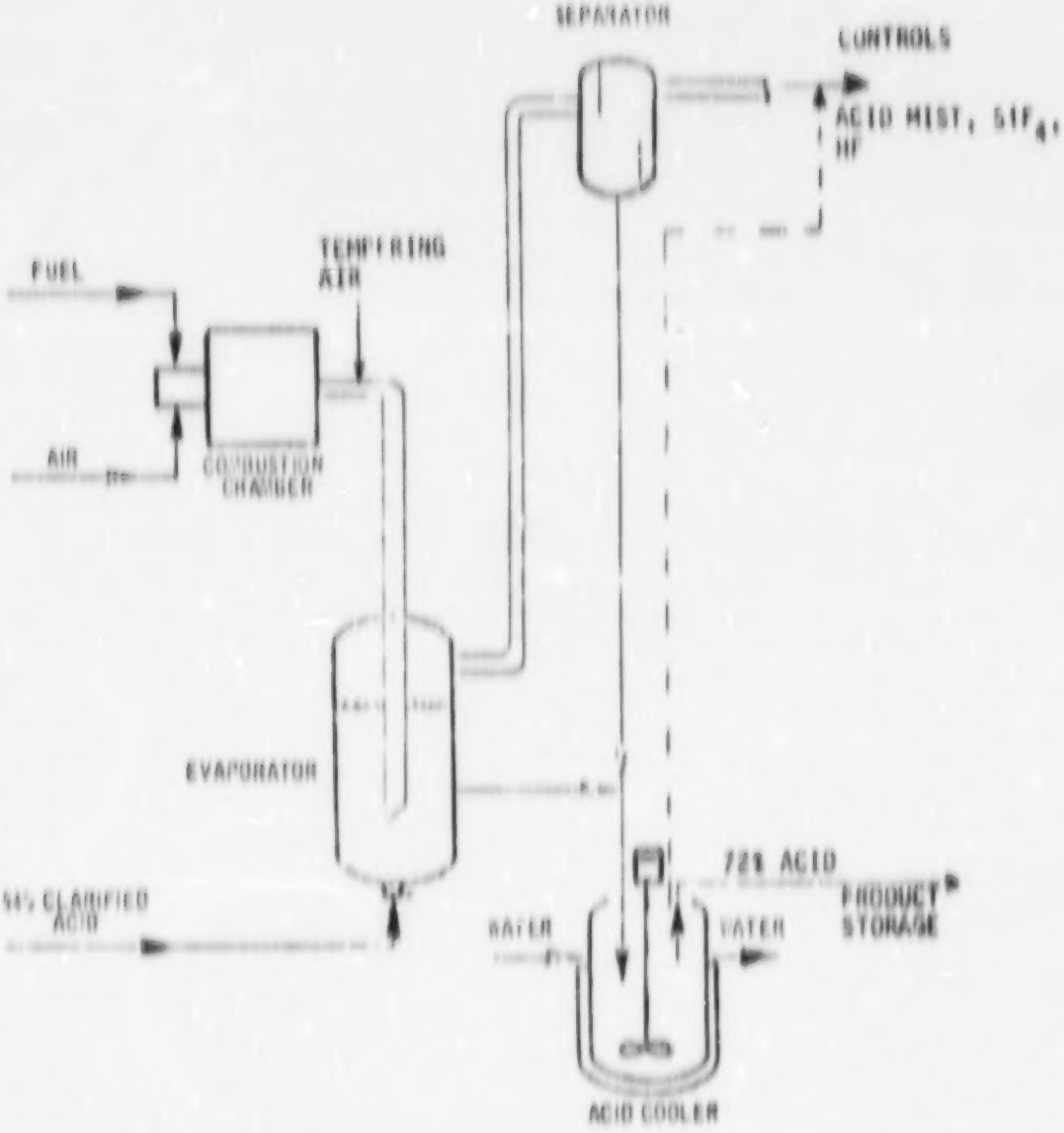


Figure 5-2: Submerged Combustion Process for Producing Superphosphoric Acid

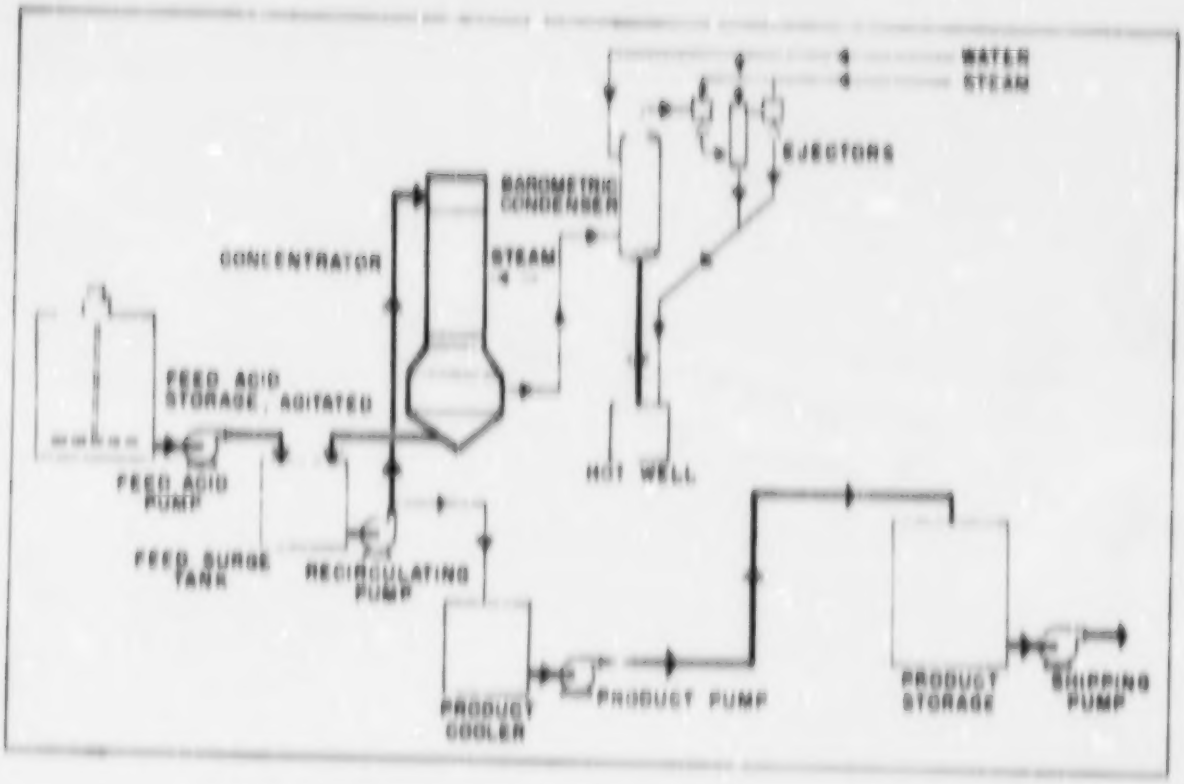


Figure 5-1: Vacuum Concentration Process for Producing Superphosphoric Acid (Reprint with Permission of the Sulfur Institute from Phosphate Fertilizers, 1966, p. 21)

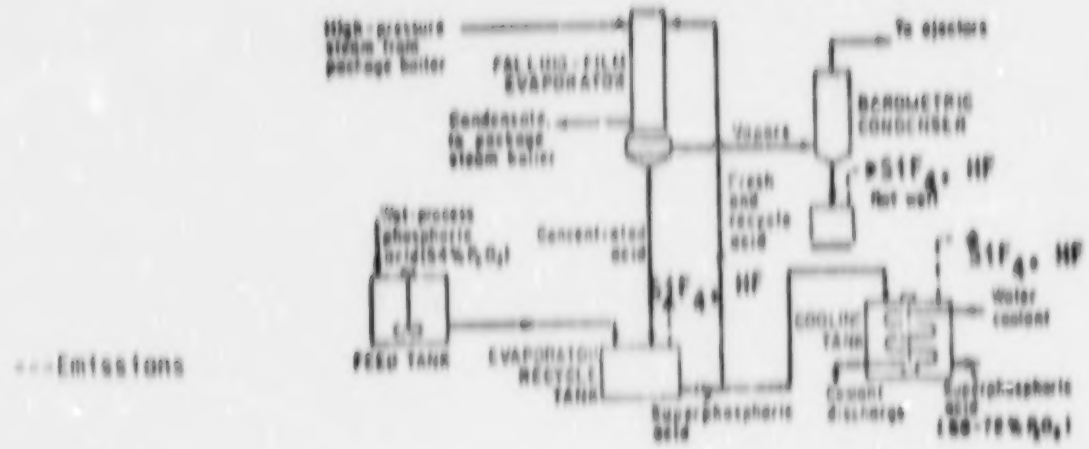


Figure 5-4: Falling Film Process

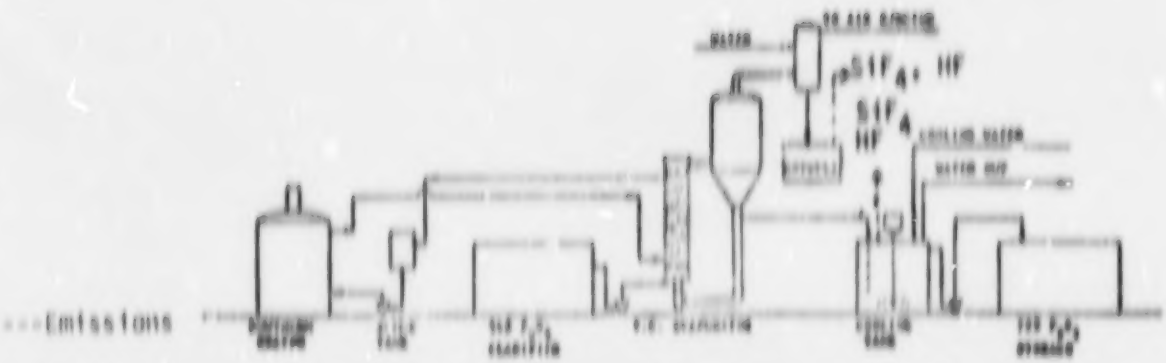


Figure 5-5: Forced-Circulation Evaporation Process

the acid film moves down along the inside wall of the tubes where evaporation occurs. The concentrated acid separates from the water vapor in a flash chamber at the bottom of the evaporator, product acid flows to the evaporator recycle tank, and vapors go to the barometric condenser. The process off-gases to the condenser consist of steam, SiF_4, and HF. After condensation, these materials flow to a hotwell for cooling and subsequent draining to the gypsum pond. Concentrated acid is continuously drawn from the evaporator to product cooling tanks before being pumped to storage.

In the forced-circulation evaporation process shown in Figure 5-5, 54% P_2O_5 feed acid is mixed with concentrated acid as it is pumped into the concentrator system. Evaporation and subsequent separation from the water vapor take place as the acid leaves the heated tube bundle and enters the vapor head. The vapor is vented to a barometric condenser and the acid flows toward the bottom of the vapor head tank. Part of the acid is removed to the cooling tank and the remainder is recycled to the tube bundle.

5.2.2 Emission Sources

The source of atmospheric emissions and, to some degree, the quality of emissions from superphosphoric acid plants vary with the type of process used.

5.2.2.1 Emissions from Submerged Combustion Process

The major source of fluoride emissions from the submerged combustion process is the evaporator. These emissions consist of SiF_4 and HF in concentrations depending on the fluoride content of the acid feed and the final concentration of phosphoric acid produced.

Control of the evaporator off-gases is complicated by the presence of entrained and volatilized phosphoric acid which may be recovered by an entrainment separator and recycled to the process. The acid vapor and fume which leaves the separator forms an aerosol which is difficult to control in anything less than a high pressure drop device. Some soluble fluoride will be contained in this mist, probably proportional in concentration to the fluoride contained in the feed acid.

The acid sump and product holding tank are secondary sources of fluoride emissions from the submerged combustion process. All process emissions are shown in Figure 5-6. Uncontrolled emissions from this process range from 13 to 27 pounds of fluoride per ton of P_2O_5 input.[6]

5.2.2.2 Emissions from Vacuum Evaporation Processes

There are three main sources of fluoride emissions from the vacuum evaporation process: the barometric condenser hotwell, the

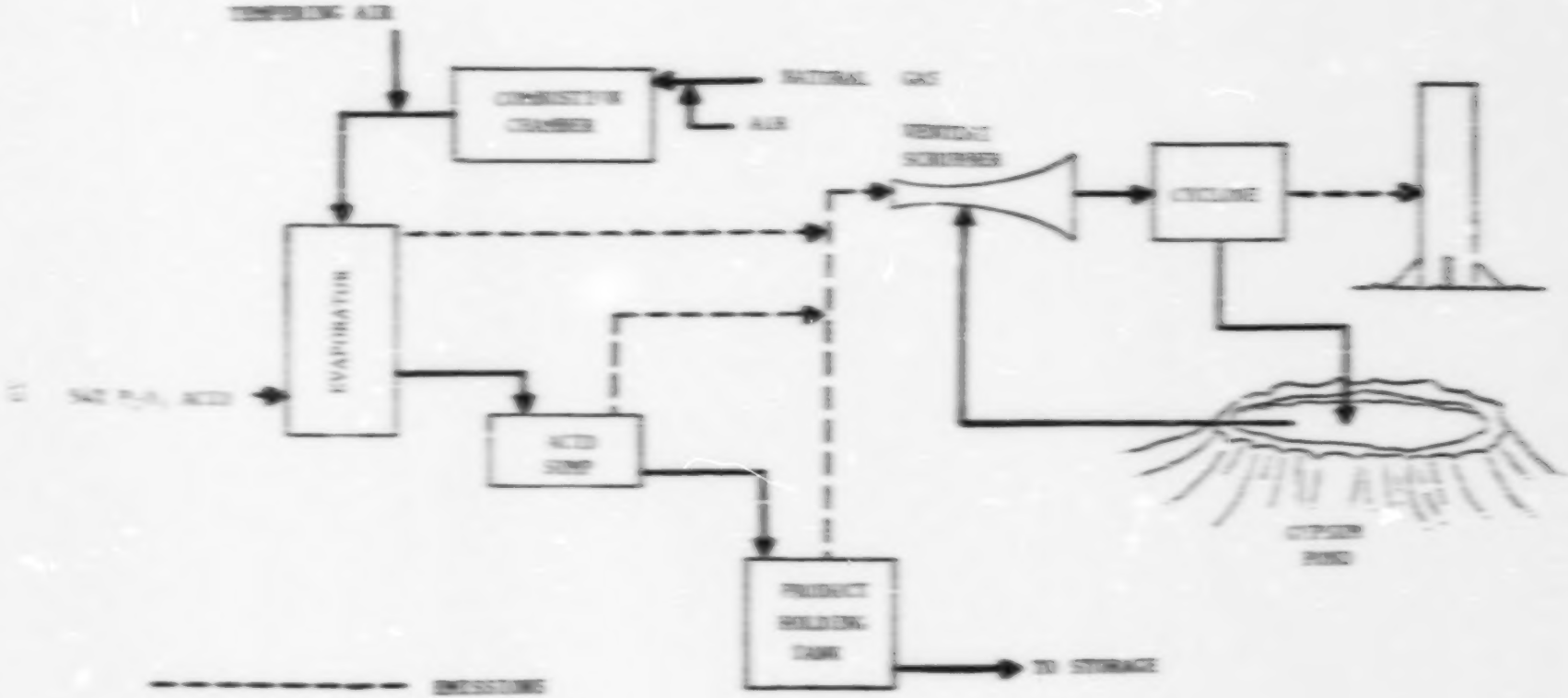


Figure 5-6: Sabeneja Dehydration Superphosphoric Acid Production

evaporator recycle tank, and the product cooling tank. These sources are shown in Figure 5-4 and Figure 5-5. Most of the fluorides evolved during evaporation are absorbed by the cooling water in the barometric condensers so that atmospheric emissions from this source are negligible under normal operating conditions. Non-condensibles flow to the hotwell with the condenser water, making the hotwell the major source of process emissions.

Minor sources of fluoride emissions include the evaporator recycle tank and the product cooling tank. Total fluoride emissions for an uncontrolled plant have been estimated at 0.005 pounds per ton P_2O_5 input.[7]

5.2.3 Control Equipment and Inspection Procedures

5.2.3.1 Control Equipment

Of the several types of wet scrubbers available, venturi scrubbers have found the widest application in superphosphoric acid plants. Water-induced venturi scrubbers are most frequently selected to control superphosphoric acid plant emissions because the gas flow is very low during normal operation, the gas flow may vary substantially with time, and the water-induced scrubber does not require a fan.

Generally the exhaust gases from the process evaporator in the vacuum evaporation technique are treated for the recovery of entrained acid before being sent to fluoride controls. The phosphoric acid recovery system may consist of an initial cyclonic separator followed by a baffled spray duct and a second separator. Weak phosphoric acid (30% P_2O_5) serves as the scrubbing medium in the duct. The scrubbing requirements for superphosphoric acid plants are nominal, and other types of scrubbers such as crossflow packed units, conventional venturi scrubbers, mobile packed scrubbers, and spray towers, each with an appropriate fan, are also acceptable for use in controlling fluoride emissions from superphosphoric acid plants. However, these devices are mechanically more complicated alternatives to the water-induced venturi in this application.

5.2.3.2 Inspection Procedures

Process Instrumentation

When NSPS tests are performed, process information should be collected. The inspector should obtain the process rate in terms of the phosphorous-bearing material feed rate and the equivalent P_2O_5 feed rate. The former should be obtainable directly from monitoring instrumentation.

while the latter should be determined by AOAC 11th Edition, Method 9.

The inspector should check process instrumentation and note the operating parameters being used at the time of inspection. These include the rate of clarified phosphoric acid feed to the process, and the rate of withdrawal of product acid to the product holding tanks. The P_2O_5 content of the acid should also be verified. Controls for submerged combustion processes also include the natural gas and air flows to the combustion chamber and the dilution air to the combustion stream. These parameters should also be recorded by the inspector.

If the vacuum evaporation process is being used, the absolute pressure and temperature of the evaporator should be noted, as well as the acid feed and withdrawal rates. The temperature of the barometric condenser should also be recorded.

Finally, for both processes, all tank levels, liquor flow rates, water temperatures, and power readings should be recorded.

Control Device Instrumentation

The inspector should also collect control device data when the NSPS tests are first performed. This information may then be used for reference for future inspections.

Scrubbers

The inspector should check to see that all control devices are operative and that the fans are on, except if a water-actuated venturi is being used. He should also note whether fluorine odors or visible emissions are detectable from the control device. He should read the total pressure drop across the process scrubbing system from a manometer or from gauges on the scrubber instrument panel, check the water flow rate into the scrubber, and make note of any observed leaks or broken seals. The pH of the scrubbing medium should also be recorded.

5.3 Diammonium Phosphate (DAP) Plants

5.3.1 Process Description

Diammonium phosphate is manufactured from phosphoric acid and ammonia. The process consists of three basic steps: reaction, granulation, and finishing operations such as drying, cooling, and screening. These are illustrated in the general process schematic shown in Figure 5-7.

In the first step, anhydrous ammonia is reacted with phosphoric acid to form a mixture of hot liquid monoammonium phosphate (MAP)/diammonium phosphate as described by the equations:

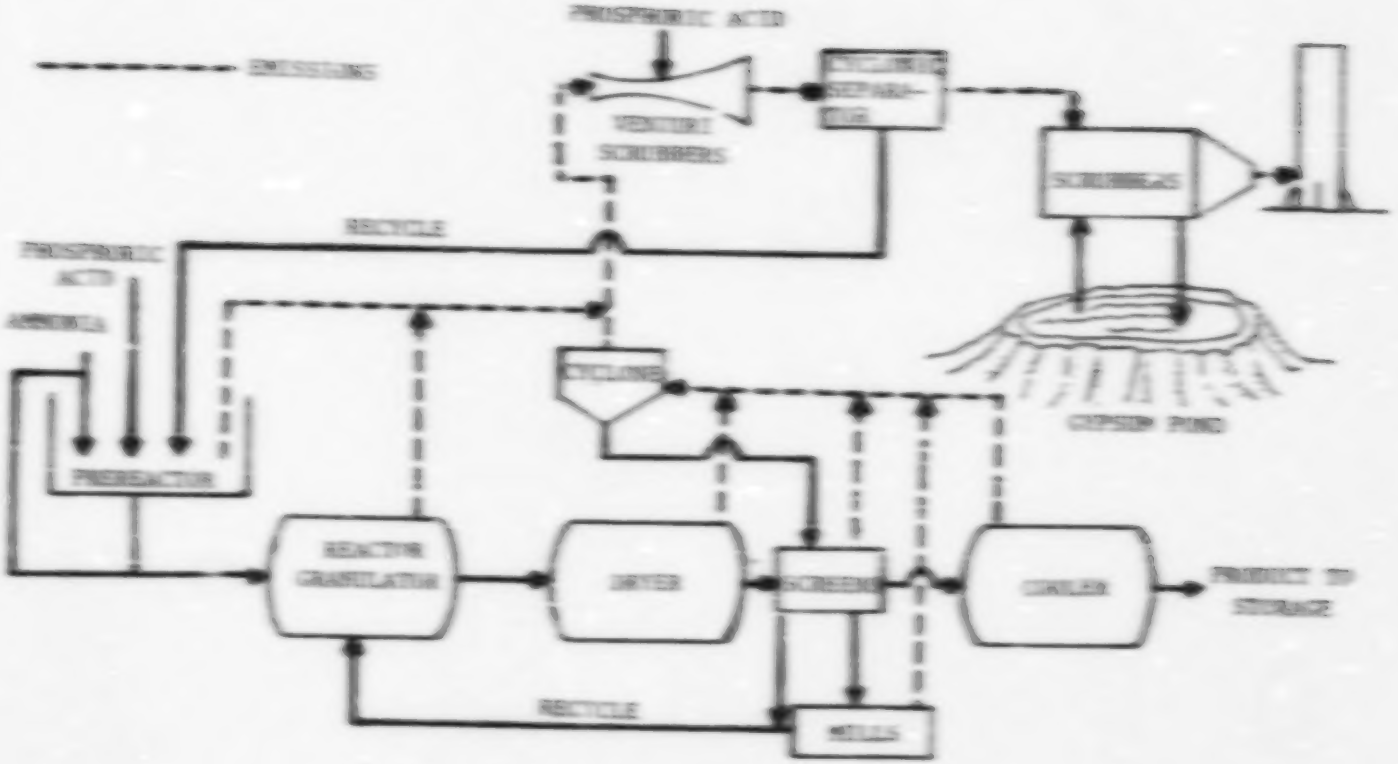


Figure 5-7: Diammonium Phosphate Production

$$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2\,H_3PO_4 \quad + 81{,}500\ BTU\ (20{,}529{,}850\ calories)$$
(gas) (liquid) (liquid) (ΔH_R @ 60°F) (5-2)

$$NH_3 + H_3PO_4 \rightarrow (NH_4)\,H_2PO_4$$
(gas) (liquid) (liquid)

The ammonia is generally obtained in bulk as a liquid under pressure, vaporized in a steam-jacketed coil, and bubbled through the liquid in a pre-neutralization reactor. Fifty-four percent phosphoric acid and 26-30% phosphoric acid are also added to the reactor to produce the slurry of MAP and DAP. The reaction is carried out using an ammonia:phosphoric acid molar ratio of about 1.3 to 1.45:1 which permits evaporation to a water content of 18-22% without thickening of the slurry to a non-flowing state.

The slurry is then pumped to the ammoniator-granulator where it is distributed over a bed of recycled fines. Additional ammonia and recycled product are added to the rolling bed of solids to bring the NH_3:Acid molar ratio up to 1.9 to 2.0 to favor the production of DAP. Solidification of the product has occurred once this ratio has been reached.

The solid effluent from the granulator drum is then sent to a rotary drier where excess moisture is driven off by contact with the flue gases. Flue gas from the drier is vented through a dry cyclone collector which collects the dust generated in the granulator-drier and returns it to a recycle belt. The granular solids discharged from the drier are then elevated to a screening arrangement for particle segregation.

A primary screen removes material from the flow stream and drops it onto the fines return conveyor. Oversized material is passed to a mill where it is ground to relatively small size and returned to the belt. Material passing the primary screen falls onto a secondary screen which rejects any fines that may have been carried over and passes the material of proper size through a cooler into a product storage drum.

All other solids are recycled back to the granulator drum where they are trapped until the particles have grown large enough for them to be classified as finished product.

Side reactions resulting from the production of ammonium phosphates produce ammonium fluoride, ammonium sulfate, and ammonium fluorosilicate. In addition, some of the fluorine is liberated as SiF_4. It should be noted that the product weight, rather than its P_2O_5 content, is the usual basis for rating a DAP plant, although the product is assayed routinely for P_2O_5.

There are two commonly used variations of the DAP manufacturing process: the Dorr-Oliver Process and the TVA (Tennessee Valley Authority) Process. In the Dorr-Oliver Process, the reaction is completed in the fluid state by using additional reactors. The slurry overflows to a turn-shaft paddlemixer containing recycling dry product. The moist granules formed in the mixer are then dried, cooled, screened, and stored. Figure 5-8 is a typical Dorr-Oliver Process flowsheet.

In the TVA Process, the slurry and recycling material are fed into a revolving drum where final ammoniation and granulation take place simultaneously. The moist granules are then dried, cooled, screened, and stored as with other processes. A flowsheet of this process is shown in Figure 5-9.

5.3.2 Emission Sources

The major sources of fluoride emissions from diammonium phosphate plants include the reactor, granulator, dryer, cooler, screens, and mills. These sources are shown in Figure 5-7.

The preneutralization reaction that occurs in the reactor generates a large quantity of heat which raises the temperature of the reactants and results in the emission of water vapor, ammonia, and SiF_4 with the discharge gas stream. In the granulator, the ventilating air flow purges a substantial amount of ammonia along with some water vapor and DAP dust. There is very little evolution of fluorine-containing gases from the granulator because of the high concentration of ammonia in the vapor phase.

Reactor-granulator gases are treated for ammonia recovery in a scrubber using phosphoric acid as a scrubbing medium. The acid reacts with the ammonia and the resulting product is recycled back to the process. Fluorides, which can be stripped from the acid, are usually controlled by a secondary scrubber.

Drier emissions consist of ammonia, fluorides, and particulate. Gases are sent through a cyclone for product recovery before being treated for ammonia or fluoride removal.

Emissions from the screens, mills, and cooler consist primarily of particulate and gaseous fluorides. Very little volatile material is given off in the cooler because the temperature is reduced and the vapor pressure of each of the gaseous species is decreased. All gases are treated for product recovery before entering fluoride control equipment. Approximately 0.3 pounds of fluorides per ton P_2O_5 are emitted by the reactor and granulator, and about 0.3 pounds of fluoride per ton P_2O_5 are evolved from the dryer, cooler, and screens.[5] One plant producing 17 tons ammonium phosphate per hour has been successful in reducing its total fluoride emissions from the DAP process to 16.4 pounds/day using a

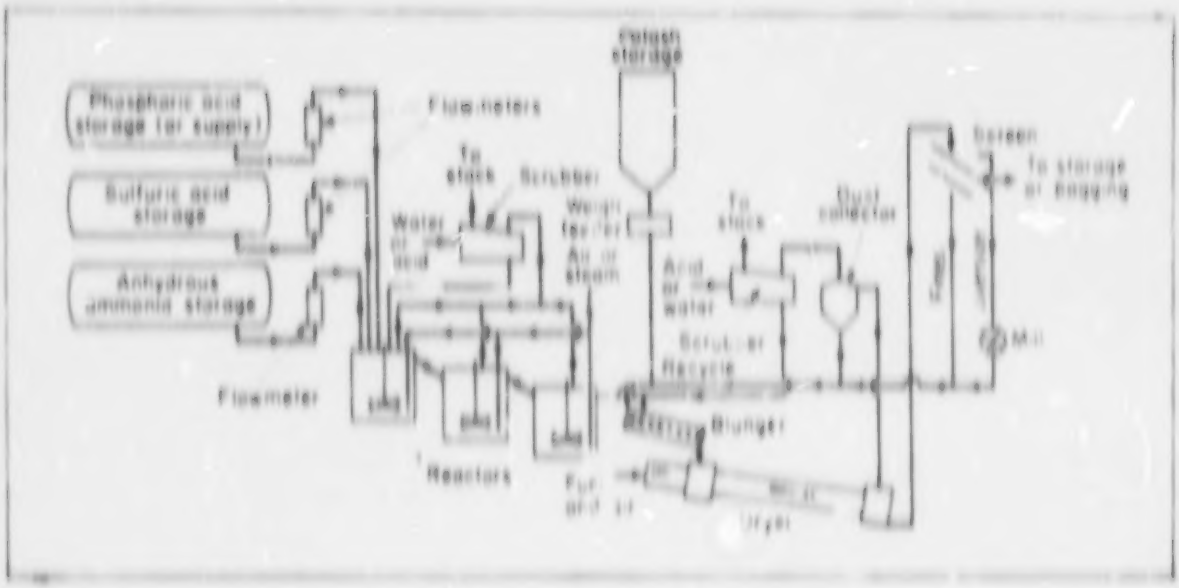


Figure 5-8: Dorr-Oliver Process (Reprint with Permission of the Sulfur Institute from Phosphatic Fertilizers, 1966, p. 16)

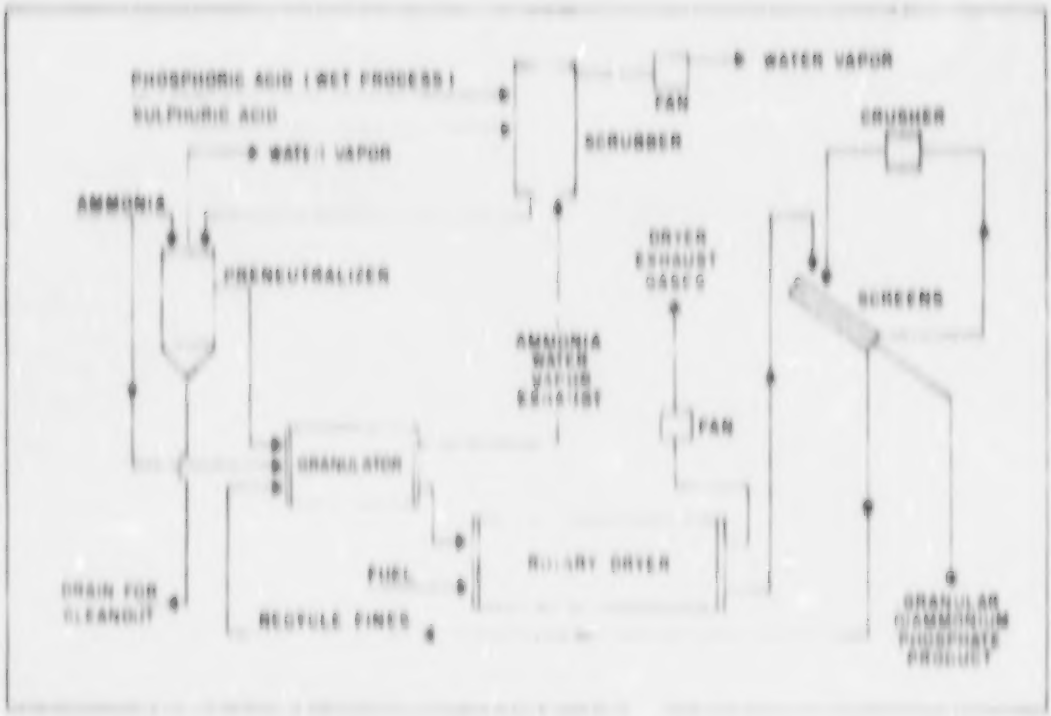


Figure 5-9: T.V.A. Process (Reprint with Permission of the Sulfur Institute from Phosphatic Fertilizers, 1966, p. 17)

cyclonic spray scrubber. There is also a substantial fugitive dust problem due to the mechanical handling of granular solids. Transfer and screening of the solid product and recycle solids cause some generation and dispersion of product dust which contains a small amount of fluorine as an impurity.

5.3.3. Control Equipment and Inspection Procedures

5.3.3.1 Control Equipment

The three major sources of atmospheric emissions in DAP plants are treated exclusively by wet scrubbers, largely because of the necessity for removal of both gaseous and particulate emissions and the presence of relatively high humidity in the gas streams. The combination of requirements for particulate collection and gas absorption for NH_3 recovery and fluorine emission control permits the application of a wide variety of scrubber types for DAP plant service.

Venturi scrubbers are the key control devices used in DAP plants, whereas impingement scrubbers have had only limited success in these plants because of small particle size. Venturi and cyclonic scrubbers are generally used to recover ammonia from the reactor/granulator and the dryers. Cyclones and wet scrubbers are also used to remove particulate from the cooler stream. Although additional scrubbers for fluoride removal are common, the are not typically found.

5.3.3.2 Inspection Procedures

Process Instrumentation

Process information should be collected when NSPS tests are performed. The inspector should obtain the process rate in terms of the phosphorous-bearing material feed rate and the equivalent P_2O_5 feed rate. The former should be obtainable directly from monitoring instrumentation, while the latter should be determined by Method 9 in the 11th Edition of AOAC.

The inspector should check process instrumentation and note the operating parameters being used at the time of inspection. These include the ammonia and phosphoric acid feed rates, the reaction and dryer temperatures, and the product rate to storage.

Finally, all tank levels, flow rates, and power readings should be recorded.

Control Device Instrumentation

The inspector should also collect control device data when the

NSPS tests are first performed. This information may then be used for reference for future inspections.

The inspector should check to see that all control devices are operative and that the fans are on, except if a water-actuated venturi is being used. He should also note whether fluorine odors or visible emissions are detectable from the control device. He should read the total pressure drop across the process scrubbing system from a manometer or from gauges on the scrubber instrument panel, check the water flow rate into the scrubber, and make note of any observed leaks or broken seals. The pH of the scrubbing medium should also be recorded.

5.4 Run-of-Pile Triple Superphosphate (ROP-TSP) Plants

5.4.1 Process Description

The run-of-pile triple superphosphate process is essentially very simple and requires a minimum amount of process equipment. Measured quantities of ground rock and 52-54% P_2O_5 phosphoric acid are mixed at ambient temperature to form a viscous slurry. Most plants in the United States mix the slurry in a TVA cone mixer, which has no moving parts. Mixing is accomplished by the swirling action of rock and acid streams introduced simultaneously into the cone. The reactions that take place during mixing are described by the equations:

$$Ca_{10}(PO_4)_6F_2 + 42H_3PO_4 + 30H_2O \rightarrow 30CaH_4(PO_4)_2 \cdot H_2O + 6HF \quad (5-3)$$

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$$

$$H_2SiF_6 + 2HF \rightarrow SiF_4$$

After mixing, the slurry is dropped onto a slowly-moving belt, or den, where it solidifies, as shown in the process schematic in Figure 5-10. The porous mass is reduced to small chunks by a cutter at the end of the belt and then conveyed to a storage pile for curing. The reaction continues in the storage pile and is considered complete after about 30 days. The product is then considered cured and ready for shipment.

5.4.2 Emission Sources

Emissions of fluorides and particulates occur during the production, conveying, and storage of run-of-pile triple superphosphate. The main sources of fluoride emissions from ROP plants include the mixing cone, curing belt (den), transfer conveyors, and storage piles, also shown in Figure 5-10.

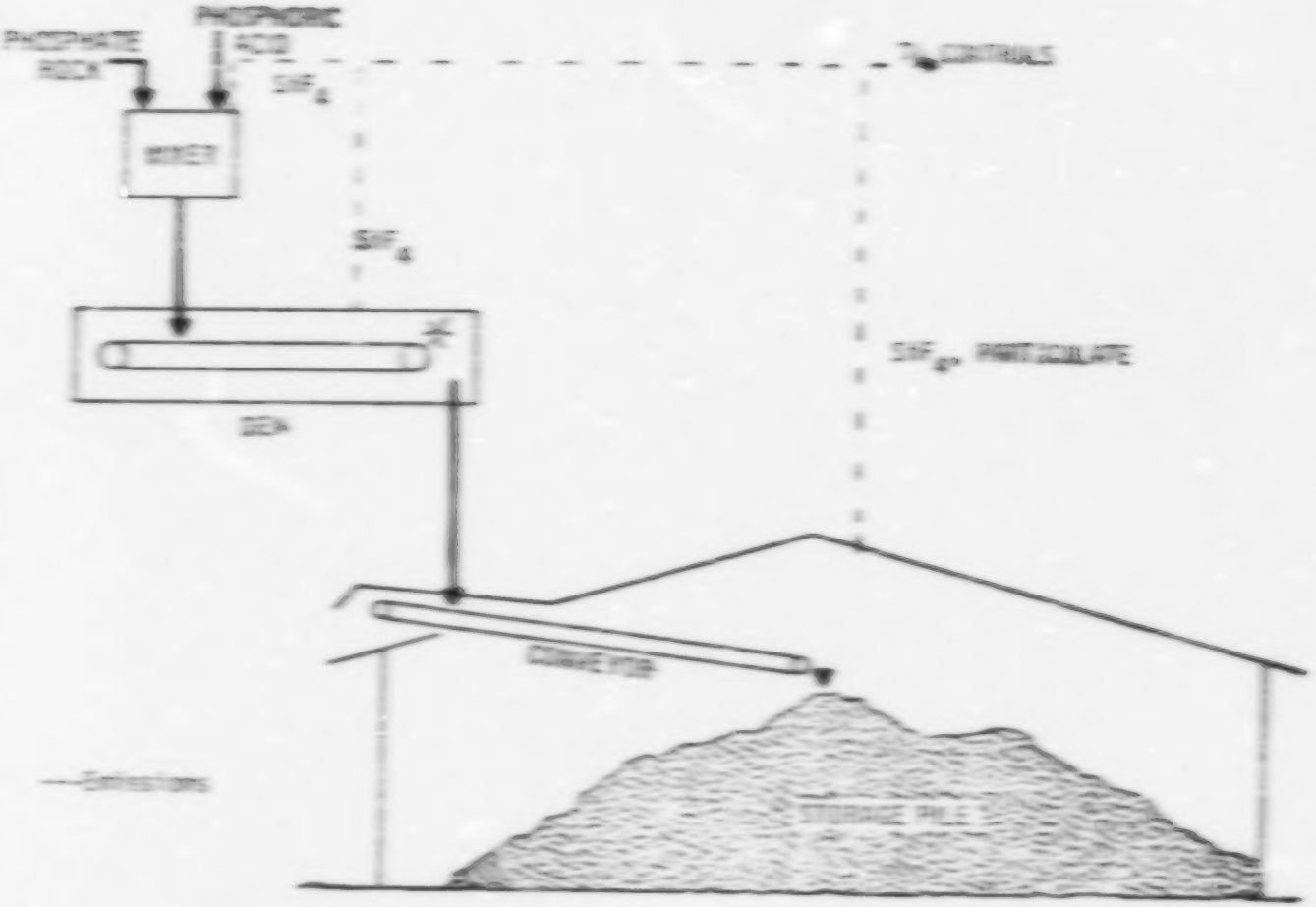


Figure 5-10: Run-of-Pile Triple Superphosphate Production and Storage

Fluoride emissions are primarily silicon tetrafluoride, 35-55% of the total fluoride content of the acid and rock being volatilized as SiF_4. Distribution of emissions among these sources will vary depending on the reactivity of the rock and the specific operating conditions employed. Obviously, emissions from the storage pile are greater when the pile is being rearranged than when it has lain undisturbed for an extended period of time.[9]

Fluoride emissions from ROP-TSP production and storage have been estimated at 31-48 pounds per ton of P_2O_5.[10] Typical controlled emissions from plants which control production and storage areas can range from 0.2 to 3.1 pounds of fluoride per ton of P_2O_5.[11,12] One existing ROP-TSP plant producing 59,000 lbs/hr has controlled its fluoride emissions to 1.49 lbs/hr using 97% efficient venturi and cyclonic scrubbers.

5.4.3 Control Equipment and Inspection Procedures

5.4.3.1 Control Equipment

According to NSPS, run-of-pile plants are subject to the standards of performance for triple superphosphate plants, which include any combination of mixers, curing belts, reactors, granulators, dryers, cookers, screens, mills, and facilities which store run-of-pile triple superphosphate. NSPS regulates only fluoride emissions from these facilities. The best demonstrated control of fluoride consists of scrubbing emissions with water.

Venturi scrubbers and cyclonic spray tower scrubbers with a packed bed section are used as primary and secondary controls respectively. These have been successfully applied to the mixing cone, den, transfer conveyor, and storage pile in ROP-TSP plants.

5.4.3.2 Inspection Procedures

Process Instrumentation

Process information should be collected when NSPS tests are performed. The inspector should obtain the process rate in terms of the phosphorous-bearing material feed rate and the equivalent P_2O_5 feed rate. The former should be obtainable directly from monitoring instrumentation, while the latter should be determined by Method 9 in the 11th Edition of AOAC.

The inspector should check process instrumentation and note the operating parameters being used at the time of inspection. These include the ground phosphate rock feed rate, the phosphoric acid feed

rate, the rate of product feed to storage, the amount of ROP in storage, and the age of ROP in storage.

Control Device Instrumentation

The inspector should also collect control device data when the NSPS tests are first performed. This information may then be used for reference for future inspections.

The inspector should check to see that all control devices are operative and that the fans are on, except if a water-actuated venturi is being used. He should also note whether fluorine odors or visible emissions are detectable from the control device. He should read the total pressure drop across the process scrubbing system from a manometer or from gauges on the scrubber instrument panel, check the water flow rate into the scrubber, and make note of any observed leaks or broken seals. The pH of the scrubbing medium should also be recorded.

5.5 Granular Triple Superphosphate (GTSP) Plants

5.5.1 Process Description

Triple superphosphate (also called treble, double, or concentrated superphosphate) is an impure monocalcium phosphate made by reacting phosphoric acid with phosphate rock. Although it may be made with any phosphoric acid, the major portion of this material is now made with wet process phosphoric acid. The P_2O_5 equivalent of the product ranges from 44-52 percent, depending on the purity of the acid and rock and the efficiency of the manufacturing process.

Three processes are currently in use for the direct production of granular triple superphosphate. These are the TVA Process, the Dorr-Oliver Process; and the process which uses cured ROP-TSP.

A process schematic for the TVA, one-step granular process, is shown in Figure 5-11. In this process, ground phosphate rock and recycled process fines are fed into the acidulation drum along with concentrated phosphoric acid and steam, which helps to accelerate the reaction and ensure an even distribution of moisture in the mix. The mixture is discharged into the granulator where solidification occurs, passes through a rotary cooler, and is screened. Over-sized material is crushed and returned to the process with undersized material. The process reactions are described by the equations:

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10H_2O \rightarrow 10CaH_4(PO_4)_2 \cdot H_2O + 2HF \quad (5\text{-}4)$$

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$$

$$H_2SiF_6 \rightarrow 2HF + SiF_4$$

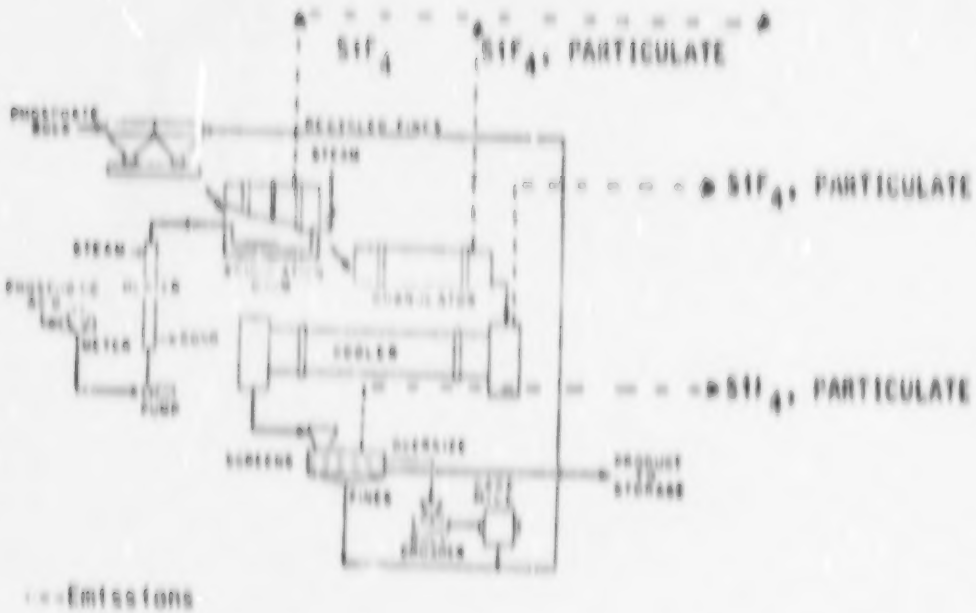


Figure 6-11: T.V.A. One-Step Process for Granular Triple Superphosphate

In the Dorr-Oliver slurry granulation process shown in Figure 5-12, phosphate rock is mixed with 40% P_2O_5 phosphoric acid in a series of mixing tanks to form a slurry. A thin slurry is continuously removed and mixed with a large quantity of dried, recycled fines in a pugmill mixer, where it coats out on the granule surfaces and builds up the granule size. The granules are dried and screened and mostly recycled back into the process.

In a somewhat similar process, cured ROP-TSP is used to produce GTSP. The ROP-TSP is treated with water and steam in a rotary drum and then dried and screened.

After manufacture, the product is sent to a storage building by a conveyor belt which discharges the material into bins or piles for curing. The GTSP is held approximately 30 days to stabilize the composition, after which it is considered cured and ready for shipping. Front-end loaders move the GTSP to elevators or hoppers where it is conveyed to screens for size separation. Over-sized material is rejected, pulverized, and returned to the screen, while undersized material is returned to the GTSP production plant. Material within specification is shipped as product.

5.5.2 Emission Sources

Sources of atmospheric emissions from granular triple superphosphate plants include all major process components. For plants using the TVA, one-step process, those are the acidulation drum, the granulator, the cooler, and the screening and crushing operations. These are indicated in Figure 5-11. The mixing tanks, the pugmill mixer, the dryer, and the screens are the major sources for the Dorr-Oliver process, as shown in Figure 5-12. Fluorides are emitted from the granulator, mixer, dryer, screens, and mills in both gaseous and particulate form.

The acidulation drum and granulator (TVA Process) and the mixing tanks and pugmill mixer (Dorr-Oliver Process) account for about 30% of the fluoride emissions; the dryer and screens account for 50%, and the storage facilities account for the remainder. It has been estimated that an uncontrolled facility would emit 21 pounds of fluorides per ton of P_2O_5 input.[3]

One plant, which produces 84,100 lbs triple superphosphate per hour, has been able to control its fluoride emissions to 17.1 lbs per day. Control equipment at this plant consists of a cyclonic spray scrubber with efficiencies better than 90%.

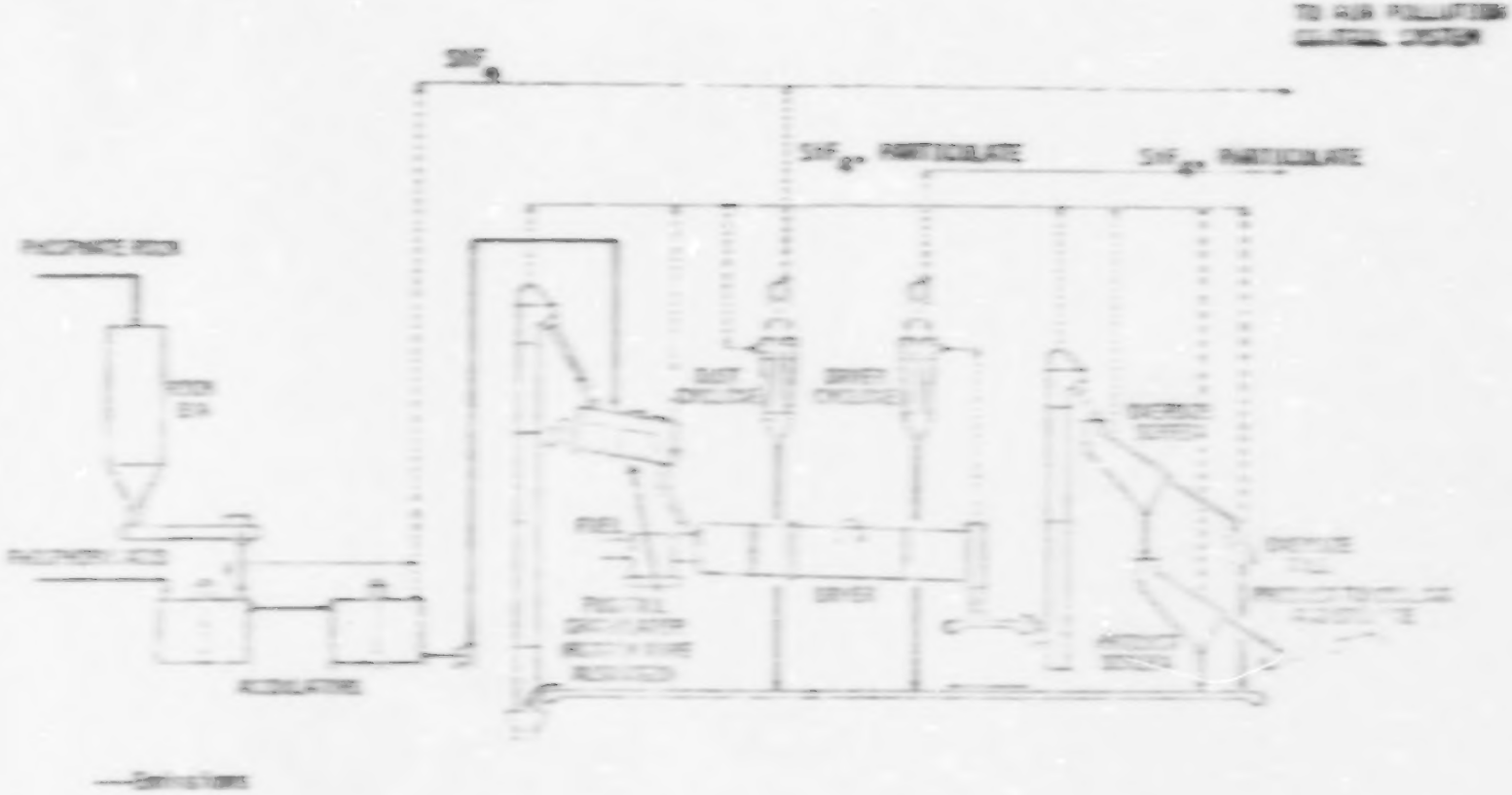


Figure 5-12: Den-Other Slurry Granulation Process for Triple Superphosphate

5.5.3 Control Equipment and Inspection Procedures

5.5.3.1 Control Equipment

Fluorides in both gaseous and particulate form are the only significant air pollutants emitted by granular triple superphosphate plants. Process emissions from these plants are generally treated by wet scrubbers. The dust generated by solids handling and the fluorine evolved by curing of the TSP product can be treated separately by use of a fabric collector and a cyclonic or packed scrubber or simultaneously by a scrubber which serves both functions.

5.5.3.2 Inspection Procedures

Process Instrumentation

Process information should be collected when NSPS tests are performed. The inspector should obtain the process rate in terms of the phosphorous-bearing material feed rate and the equivalent P_2O_5 feed rate. The former should be ootainable directly from the required process monitoring instrumentation, such as that shown in Figure 5-13, while the latter should be determined by the Spectrophotometric Molybdovanadophosphate Method, Method 9 in the 11th Edition of AOAC.

The inspector should check process instrumentation and note the operating parameters being used at the time of inspection. More specifically, he should be concerned with the phosphate rock and phosphoric acid feed rate, and the rate of product feed to storage.

Control Device Instrumentation

The inspector should also collect control device data when the NSPS tests are first performed. This information may then be used for reference for future inspections.

The inspector should check to see that all control devices are operative and that the fans are on, except if a water-actuated venturi is being used. He should also note whether fluorine odors or visible emissions are detectable from the control device. He should read the total pressure drop across the process scrubbing system from a manometer or from gauges on the scrubber instrument panel, check the water flow rate into the scrubber, and make note of any observed leaks or broken seals. The pH of the scrubbing medium should also be recorded.

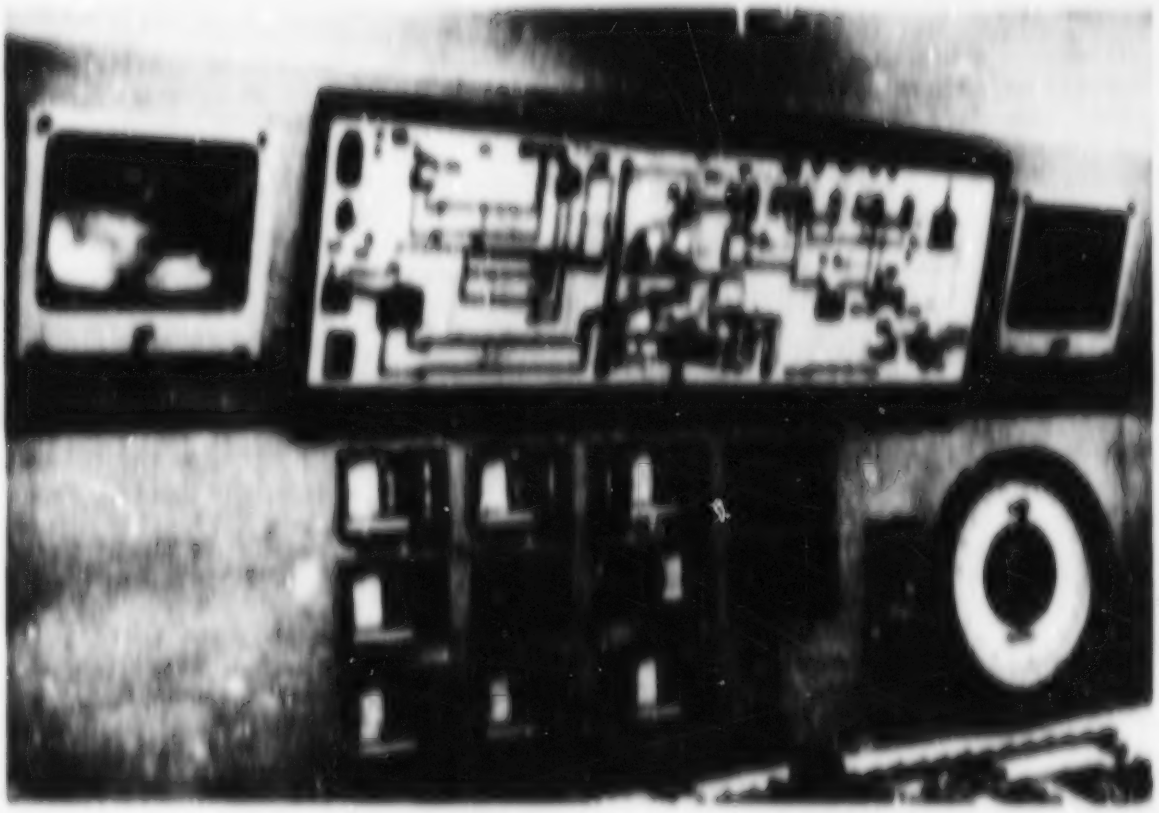


Figure 5-13: Control Panel for GTSP Plant

SECTION 6

FACILITY RECORDKEEPING AND REPORTING REQUIREMENTS

6.1 Recordkeeping

NSPS for all phosphate fertilizer plants require that the equivalent P_2O_5 feed be recorded daily. This should be determined by Method 9 in the 11th Edition of AOAC and entered in a logbook for compilation. All analytical data and calibrations should be kept on record. Triple superphosphate storage facilities must maintain an accurate account of triple superphosphate in storage to permit the determination of the amount of equivalent P_2O_5 stored. Furthermore, they must maintain a daily record of total equivalent P_2O_5 stored.

Control device monitoring instrumentation must continuously measure and permanently record the total pressure drop across the scrubbing system. These records should be dated and all records and calibration information kept in the event that they are needed to verify emission levels.

Finally, NSPS require that the mass flow of the phosphurous-bearing feed material to the process be monitored and calibrated. This material should be dated and kept on record for possible future use to verify production and emissions.

6.2 Reporting Procedures

Although the NSPS do not require periodic submittal of data or data summaries, they do require that any plant owner or operator submit the results of a performance test performed within 60 days after achieving the maximum production rate at which the facility will operate, but not later than 180 days after initial startup. Furthermore, a record of the occurrence and duration of any startup, shutdown, or malfunction in the operation of any affected facility shall be kept for a period of two years.

SECTION 7

INSPECTIONS

Plant inspections enable the inspector to determine the status of the plant's emissions and air pollution control equipment. The initial inspection should take place during the performance test while follow-up inspections may take place on a regular basis thereafter. Inspections during the performance test will ensure that the tests are conducted under the proper operating conditions and that the correct test procedures are used. Comparison of operating parameters observed during subsequent inspections with those recorded during the performance test should indicate whether emissions are within limits specified by NSPS.

7.1 Inspection Preparation

In preparation for all inspections, the inspector should familiarize himself with the plant processes, the inspection points and the control equipment. He should review plant files for process and control equipment details and enforcement history. The schematics of air pollution control systems should be prepared at this point in order to simplify field inspection. He should also obtain inspection checklists and the necessary safety and inspection equipment, including the following:

Safety Equipment	Inspection Equipment
Hard hat	Tape measure
Safety glasses	Flashlight
Steel-toed shoes	Thermometer
Respirator with cartridge (for acids, bases, and NH_3)	Manometer
Gloves	Velometer
Coveralls	RPM indicator

As part of the inspection preparation, the inspector and plant personnel should discuss the process and control data that are required to complete the inspection checklists. If the plant considers any of this data proprietary information, the inspector should assure the plant that the information will be treated as confidential and that it will be stored in a separate confidential file.

Plants may request that information given to an EPA inspector

be treated as confidential in accordance with Part 2, Sub-part B of Chapter I of 40 CFR. This request for confidentiality should be made at the time that the information is exchanged.

7.2 Performance Test

During the performance test, the inspector must observe both the process and control equipment operation and the emission tests themselves. He must be sure that the tests are conducted under the proper operating conditions and that the proper test procedures are being used. The performance test will determine whether the emission standards will be met when the plant is operating under normally-encountered conditions that produce maximum emissions. Furthermore, values for key process and control equipment operating parameters can be obtained to form a basis of comparison for future plant inspections.

7.2.1 Pre-Test Procedures

Prior to the actual performance test, the inspector should arrange a meeting with plant personnel to review details of the New Source Performance Standards and the applicable testing procedures. The inspector should be prepared to provide copies of the Performance Standards at this meeting if they are needed. He should also inform all parties of the latest revisions to the Standards. At this time, the unit(s) to be tested should be properly identified and located on a plant or process plan.

The inspector, testing crew, plant personnel, and all parties concerned with the performance test should hold a meeting prior to the beginning of the tests. The inspector should make clear that he is there to monitor the tests and that he will do so as unobtrusively as possible. He should inform all members of the test party that, if he sees techniques or equipment used not conforming with the test requirements specified in the Standards of Performance for New Sources, he will make note of his observations and advise the person in charge of conducting the test. He should make it clear that he will not interfere with or pre-empt any contract agreement between the owner and the test company, but will simply make his observations known and note them.

A number of process operating parameters must be established during the performance tests. These include the mass flow of phosphorous-bearing feed material to the process, the equivalent P_2O_5 feed, and the control equipment operating parameters. The inspector should inform the testing crew as to which process parameters should be recorded during the tests.

7.2.2 Performance Test Monitoring

Important process and emission control device operating conditions should be recorded during the compliance test to provide a baseline for comparison with operating conditions observed during later inspections. Such information may also indicate reasons for excessive emissions if the source fails to meet NSPS.

The inspector should observe process operation during the emission tests to ensure the validity of the data for use in assessing plant performance and compliance. He should also complete the performance test checklist shown in Table 7-1. Any additional parameters or observations that are related to emissions should also be recorded.

As required by 60.8 of 40 CFR, the plant operator shall furnish EPA a written report of the emission tests. These reports should be carefully checked and the data compared with values on the inspection checklist.

7.3 Post-Performance Test Inspections

Regular visits to the plant enable the inspector to determine the condition of the plant's emission controls and their compliance status. Comparison of operating parameters observed during periodic inspections with those recorded in the performance test should indicate whether or not the source is in compliance.

Although the frequency of inspection is often governed by regulatory agency policy, a quarterly inspection is recommended unless complaints necessitate more frequent visits. The major emphasis of the inspection is placed on checking facility records and observing process and control equipment operation. The inspector should compare records of operating hours and process rates to those recorded in the performance test. Control device and process instrumentation give an indication of fluoride emissions.

7.3.1 Pre-Inspection Procedures

Because the major emphasis of the inspection is placed upon checking facility records and observing process and control equipment operation, the inspector should familiarize himself with plant processes and the New Source Performance Standards prior to his visit. He should read the performance test report and become familiar with the operating parameters under which the test was conducted. Furthermore, he should obtain from the plant or appropriate regulatory agency a schematic of the emission control equipment and should make himself thoroughly familiar with the control system. This is an important step because fluoride emission control equipment at phosphate fertilizer plants tends to be a a complex system of control devices.

TABLE 7-1

NSPS INSPECTION CHECKLIST FOR PHOSPHATE FERTILIZER PLANTS
DURING PERFORMANCE TEST

Facility Name _____

Facility Location _____

Name of Plant Contact _____

Source Code Number _____

Unit Identification (to be tested) _____

Design Feed* Rate _____ tons/day**

Actual Feed* Rate _____ tons/day**

Initial Start-up Date _____

Continuous Operation Date _____

Test Date _____

Type of Plant (See Table 7-2, Page 66) _____

A. PRE-TEST DATA (OBTAIN FROM TEST FIELD LEADER)

Test Company _____

Field Leader _____

Duct Dimensions _____ in. x _____ in; Area _____ ft²

Nearest Upstream Obstruction _____ ft

Nearest Downstream Obstruction _____ ft

Number of Sampling Ports _____

Number of Sampling Points _____

Number of Sampling Points Required
from Figure 1-1 in 40 CFR 60 _____

* Feed of phosphorous-bearing materials
** Record on a separate sheet if company confidential information and retain in confidential file

TABLE 7-1 (continued)

B. PROCESS

Loading Method ☐ Batch ☐ Continuous

Operating Schedule _____ hr/day _____ days/wk _____ wk/yr

Actual Feed Rate _____ tons/hr

Equivalent P_2O_5 Feed Rate _____ tons/hr

Air Pollution Control System Schematic

1. Processes controlled by system (drying, conveying, mixing, etc.):

2. Indicate test points on schematic.

C. PROCESS INSTRUMENTATION

Mass-flow Monitoring Device:

Description:

Reading:**

Is calibration within ±5% over operation range?

Scrubbing System:

Water Usage Rate: _____ gal/min

Pressure Drop: _____ inches H_2O

Gas Volumetric Flow Rate: _____ ICFM

Stack Temperature: _____ °F

Liquid-to-Gas Ratio: ____ gallons/SCFM

** Record on a separate sheet if company confidential information and retain in confidential file

TABLE 7-1 (continued)

D. FLUORIDE PERFORMANCE TEST

Test Number _____ Start Time _____ Finish Time _____

	Yes	No
Preliminary Traverse Run (Method 1) Chosen Nozzle Diameter _____ in.	☐	☐
Train Leak Check	☐	☐
Stack Pressure	☐	☐
Stack Temperature	☐	☐
Moisture Determination (Method 4)	☐	☐

Moisture Content _____ %

ml Collected/Gas Volume _____ ml _____ ft^3

Dry Gas Meter Reading Before Test _____ ft^3 @ _____ (time)

Dry Gas Meter Reading After Test _____ ft^3 @ _____ (time)

Volume Sampled _____ ft^3

Test Duration _____ minutes

Average of Meter Orifice Pressure Drop _____ inches

Average Duct Temperature _____ °F

Velocity Head at Sampling Point _____ inches H_2O

Orifice ΔH _____

Meter Ratio _____

Repetition Start Time _____

Repetition Finish Time _____

TABLE 7-1 (continued)

E. CLEANUP PROCEDURE

Filter Condition	☐ Dry		☐ Wet
Probe Status	☐ Unbroken		☐ Broken
Glass Connectors	☐ Unbroken		☐ Broken
Cleanup Sample Spillage	☐ None	☐ Slight	☐ Major
Sample Bottle Identification	☐ Yes		☐ No
Blank Taken	☐ Yes		☐ No

Inspector _____

Signature _____ Date _____

F. LAB ANALYSIS

7.3.2 Inspection Procedures

It is suggested that the inspector first tour the plant, observe the processes, and then monitor the instruments during actual operation. Questionable areas may be further investigated by checking records and consulting plant operators. The following areas should be checked during the inspection:

- Control Equipment

  Read pertinent gauges on scrubber and compare with values obtained during performance test. Check that all gauges are operating properly. Note presence or absence of leaks, visible or odorous emissions. Inspect equipment for corrosion and check maintenance schedule.

- Process Equipment

  Read the device which monitors the mass flow of phosphorous-bearing feed materials to the process. Read operating parameters such as reaction temperatures and water flow rates, if possible. Read tank levels and note power readings.

- Review record of hours of operation, daily loading, and production rate. Review records on control device.

The Inspection Checklist form shown in Table 7-2 is derived from the procedures described above. This Checklist should be completed for each type of plant (ROP, WPPA, etc.) within the phosphate fertilizer complex under inspection. If more than one scrubbing system is used at a single plant, Section A should be completed for each system.

7.4 Post-Inspection Procedures

At the completion of the inspection, the inspector should sign and date all inspection forms, and check to be sure that all necessary information has been recorded. He should briefly convey his findings to the plant official at the site, but he should not discuss specific violations at this time.

While it is recognized that inspectors will be subject to various regional inspection follow-up procedures, it is recommended that the inspector review all the inspection data, make his recommendations for action, and present the completed report to his supervisor within 48

TABLE 7-2

NSPS INSPECTION CHECKLIST FOR PHOSPHATE FERTILIZER PLANTS
AFTER PERFORMANCE TEST

Facility Name _____

Facility Location _____

Name of Plant Contact _____

Source Code Number _____

Type of Plant (Check One)

- ☐ Wet Process Phosphoric Acid
- ☐ Superphosphoric Acid
- ☐ Diammonium Phosphate
- ☐ Run-of-Pile Triple Superphosphate (incl. storage & handling)
- ☐ Granular Triple Superphosphate (incl. storage & handling)

Design Process Rate _____ metric ton** / hour Equivalent P_2O_5 Feed Rate _____ metric ton** / hour

Actual Process Rate _____ metric ton** / hour Equivalent P_2O_5 Feed Rate _____ metric ton** / hour

Inspection Date _____ Time _____ AM / PM

** Record on a separate sheet if company confidential information and retain in confidential file

TABLE 7-2 (continued)

A. AIR POLLUTION CONTROL EQUIPMENT

1. Scrubbing System Diagram (obtain from Plant or Regulatory Agency)

Prepare schematic of control equipment similar to Figure 6-1. Number the equipment and fill in control device parameters in the next paragraph.

a. Processes controlled by system (drying, conveying, etc.):

b. System control efficiency:

TABLE 7-2 (continued)

2. Control Device Parameters

	Scrubbing System Component (List each device shown in schematic above: cyclones, venturis, etc.)	Gas Flow Through Device	Liquid Flow Through Device	Scrubbing Solution	Solution pH	Pressure Drop Across Device	L/G Ratio or Surface/Gas Ratio (Baghouse)	Control Efficiency of Device
1.								
2.								
3.								
4.								

TABLE 7-2 (continued)

3. Observations	Yes*	No
a. Visible leaks or cracks in system	☐	☐
b. System plugged	☐	☐
c. Visible corrosion	☐	☐
d. Fluoride odors noticeable	☐	☐
e. Visible emissions	☐	☐
f. Positive pressure in storage building	☐	☐
g. Fans on	☐	☐
h. Regular maintenance schedule (describe):	☐	☐

i. Additional comments

* If "Yes" is checked for parts a-g, explain below:

TABLE 7-2 (continued)

Time _____ AM PM

B. PROCESS CONTROL EQUIPMENT

Fill in the requested information for the type(s) of plant(s) under inspection:

1. Wet Process Phosphoric Acid

a. Feed measuring device _____

b. H_2SO_4 addition rate** _____

c. Reaction temperature _____

d. Evaporator temperature _____

e. Evaporator pressure _____

2a. Superphosphoric Acid - Submerged Combustion Process

a. Acid feed measuring device _____

b. Product acid withdrawal device _____

c. Natural gas flow to combustion chamber _____

d. Air flow to combustion chamber _____

e. Dilution air to combustion stream _____

f. Coolant flow rate _____

2b. Superphosphoric Acid - Vacuum Evaporation Process

a. Acid feed measuring device _____

b. Product acid withdrawal device _____

c. Evaporator pressure _____

d. Evaporator temperature _____

e. Barometric condenser temperature _____

f. Coolant flow rate _____

** Record on a separate sheet if company confidential information and retain in confidential file

TABLE 7-2 (continued)

3. Diammonium Phosphate

   a. Ammonia feed rate** _____

   b. Phosphoric acid feed rate** _____

   c. Reaction temperature** _____

   d. Dryer temperature _____

   e. Product rate to storage** _____

4. Run-of-Pile Triple Superphosphate

   a. Ground phosphate rock feed rate** _____

   b. Phosphoric acid feed rate** _____

   c. Phosphoric acid concentration _____ %

   d. Amount of product to storage** _____

5a. Granular Triple Superphosphate - TVA One-Step Process

   a. Phosphate rock feed rate** _____

   b. Phosphoric acid feed rate** _____

   c. Product rate to storage** _____

5b. Granular Triple Superphosphate - Dorr-Oliver Process

   a. Phosphate rock feed rate** _____

   b. Phosphoric acid feed rate** _____

   c. Slurry removal rate** _____

   d. Product removal to storage** _____

** Record on a separate sheet if company confidential information and retain in confidential file

TABLE 7-2 (continued)

Time _____ AM PM

C. RECORDS

	Yes	No
1. All Plants		
a. Mass flow of phosphorous-bearing feed		
Calibration records	☐	☐
Calibration within ±5% over operation range	☐	☐
Maintenance and monitoring records	☐	☐
b. Equivalent P_2O_5 feed		
Analytical data	☐	☐
c. Pressure drop across scrubber		
Calibration records	☐	☐
Calibration within ±5% over operation range	☐	☐
Maintenance records	☐	☐
d. Plant operation		
Satisfactory since performance test	☐	☐
Satisfactory since last inspection	☐	☐
2. GTSP Plants Only		
a. Amount of GTSP in storage	☐	☐
b. Equivalent P_2O_5 stored	☐	☐

Inspector _____

Signature _____ Date _____

hours of his inspection visit. Any decisions for subsequent action should then be made by both the inspector and the supervisor.

If the facility is obviously in violation of standards, then a citation should be issued. The inspector should precisely state the reasons for issuing the citation. The citation can be given only if the plant does not maintain proper records, does not monitor the rate of phosphorous-bearing feed to the process, or does not monitor the pressure drop across the scrubber according to NSPS specifications.

If the affected facility is in compliance with standards and the plant is found to be operating and maintaining its facilities in a manner consistent with good air pollution control practice, then no further action need be taken.

If the facility is not being operated or maintained precisely in accordance with the New Source Performance Standards, but violations are not clearly evident, the inspector should conclude the inspection report with recommendations to improve specific operating or maintenance procedures. These recommendations should aim at consistence with performance test conditions and at good air pollution control practice. If these recommendations are not followed, he should request another performance test be carried out under present plant operating conditions.

Regardless of the findings, the designated plant official should be notified in writing of the inspection results and any required action on the company's part should be precisely stated.

SECTION 8

GYPSUM PONDS

NSPS for the phosphate fertilizer industry focuses on atmospheric total fluoride emissions from five fertilizer manufacturing processes and storage facilities, except for fluorides from gypsum ponds. The plants that manufacture wet process phosphoric acid, diammonium phosphate, and triple superphosphate pass a large amount of fluorides to gypsym ponds. It has been estimated that up to 85% of the fluorine originally present in the phosphate rock may find its way to the gypsum pond. The water of the gypsum pond, which is used as a scrubbing liquid in most processes, is normally acidic with a pH around 1.5. Fluoride concentrations in the gypsum ponds around the country have been found to be in the range of 2000 - 12,500 ppm. The fluoride concentration of a given pond does not continue rising but tends to stabilize. This may be due to precipitation of complex calcium silicofluorides in the pond water. There would be an equilibrium involving these complexes, hydrogen ion, and soluble or volatile dissolved fluorides.

Emissions of fluorides from gypsum ponds have been estimated, measured, and calculated. The emission rate depends on pond temperature, fluorine content of pond water, and wind speed. The emissions vary from 0.2 to 10 lbs F/acre/day. Based on studies of wet process phosphoric acid production, the plants have gypsum ponds of surface areas in the range of 0.1 - 0.4 acres per daily ton of P_2O_5. Consequently, a large plant may have a gypsum pond with surface area of 200 acres or more. This means that a gypsum pond is a major source of fluoride emissions from a phosphate fertilizer plant.

The most effective way to reduce fluoride emission from a gypsum pond would be to reduce the fluoride partial pressure. The cost effective method now known would be to increase the pH through liming. Liming to a pH of 6.1 can reduce the partial pressure of fluorides 30-fold. The indicated lime addition rate would be high, so that this control method might not be economically feasible. The cost could be reduced if a method can be found to reduce phosphoric acid loss to the gypsum pond.

In the light of a strict control of fluoride emission from phosphate fertilizer processes, the fluoride emission from the gypsum pond becomes a real challenge. Any additional reduction from these plants should be achieved through a control of gypsum pond emission. Since described control methods are not economically feasible, a study of alternative control methods would be most welcome. One useful line of environmental research could be directed at reduction of gypsum pond

emission, perhaps by precipitation of fluoride compounds in an organic complex or by covering of the pond with a hydrophobic liquid cover.

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APPENDIX

1. Standards of Performance for New Stationary Sources
2. Method 13 A,B: Determination of Total Fluoride Emission

Title 40—Protection of Environment

CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY

[FRL 333-7]

PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

Fine Subpart on of Sources in the Phosphate Fertilizer Industry

On October 22, 1974 (39 FR 37419) under section 111 of the Clean Air Act, as amended, the Administrator proposed standards of performance for five new affected facilities within the phosphate fertilizer industry as follows: Wet-process phosphoric acid plants, superphosphoric acid plants, diammonium phosphate plants, triple superphosphate plants, and granular triple superphosphate storage facilities.

Interested parties participated in the rulemaking by sending comments to EPA. The Freedom of Information Center, Rm 329 West Tower, 401 M Street, SW., Washington, D.C. has copies of the comment letters received and a summary of the issues and Agency responses available for public inspection. In addition, copies of the basic comments and Agency responses may be obtained upon written request from the EPA Public Information Center (PM 213), 401 M Street, SW., Washington, D.C. 20460 (specify Docket No. OAQPS-74-PHOS-1, Phosphate Fertilizer Industry). The comments have been carefully considered and where determined by the Administrator to be appropriate, revisions have been made to the proposed standards and the format and content of the standards of performance for the source category to which the regulations for the phosphate industry are being promulgated. The principal revisions to the proposed standards and the Agency's response to major comments are summarized below.

Performance

One comment was made that the promulgation of affected facilities in addition to the source sets out in the proposed regulations as written in the proposed regulations. As a result of the proposed regulations, each component of an affected facility would have to be considered a separate affected facility. Since this was not the intent, the affected facility definition has been amended in the promulgated regulations to clarify that the failure of a component of an affected facility to subscribe to the provisions of these regulations would be a violation of those provisions only for that component. Also, the standard for fluoride emissions from open sources has been deleted as not required by the Clean Air Act. Additionally, the definition of a diammonium phosphate plant has been changed to refer to facilities which produce diammonium phosphate by reacting phosphoric acid with ammonia, rather than to facilities which produce diammonium phosphate by reacting phosphoric acid with ammonia. This change was made to clarify that facilities which produce diammonium phosphate by reacting phosphoric acid with ammonia are subject to the proposed regulations. This was the result of a comment stating that a facility which could be expected to produce more than 50 percent (by weight) diammonium phosphate in the wet process phosphoric acid plant. The intent of the original definition of process facilities was to cover wet process phosphoric acid plants from being subject to the more restrictive standard for superphosphoric acid plants.

One commentator was concerned that a loose interpretation of the definition of the affected facility for diammonium phosphate plants might result in certain of fertilizer plants becoming subject to the standards. Therefore, the word "granulation" has been inserted before "diammonium phosphate plant" in the appropriate place in subpart V to clarify the intended meaning.

Under the standards for triple superphosphate plants in Test (b)(2), the term "by weight" has been added to the definition of "run-of-pile triple superphosphate." Apparently it was not clear as to whether "25 percent of which (plus not rabbit) will pass through a 16 mesh screen" referred to percent by weight or by particle count.

Opacity Discussion

Many commentators challenged the proposed opacity standards on the grounds that EPA had shown no correlation between fluoride emissions and plume opacity, and that no data were presented which showed that a violation of the proposed opacity standard would indicate simultaneous violation of the proposed fluoride standard. For the opacity standard to be used as an enforcement tool to indicate possible violation of the fluoride standard, such a correlation must be established. The Agency has reevaluated the opacity test data and determined that the correlation is not sufficient to support a standard. Therefore, the standard for visible emissions from diammonium phosphate plants, triple superphosphate plants, and granular triple superphosphate storage facilities have been deleted. This action, however, is not meant to set a precedent regarding the promulgation of visible emission standards. The opinion still persists that visible emissions do indicate fluoride emissions in general, the Agency will continue to set opacity standards for affected facilities where such standards are feasible and warranted based on test data.

In place of the opacity standard, a provision has been added which requires an owner or operator to monitor the total pressure drop across an affected facility's scrubbing system. This requirement will require an affected facility scrubbing system. This requirement will require the owner or operator to maintain a record of the operating conditions of the control system and will serve as an effective method for a continuous compliance with the fluoride standards.

Reference Methods 13A and 13B

Reference Methods 13A and 13B, which prescribed testing and analytical procedures for fluoride emissions, were proposed along with standards of performance for the primary aluminum industry (39 FR 37581). However, these methods have been included with the standards of performance for the phosphate fertilizer industry and the fertilizer standards are being promulgated before the primary aluminum standards. Comments were received from the phosphate fertilizer industry and the primary aluminum industry on the methods as applicable to both industries. The majority of the comments dealt with possible changes to prior tests and to equipment specifications. As a result of these comments some minor changes were made. Additionally, it has been determined that acetone causes a positive interference in the analytical procedures. Although the basis for the standard are not affected, the acetone wash has been deleted in both methods to prevent potential errors. Reference Method 13A has been revised to revised the dehydration procedure (Section 3.1.2). In its place instead of the proposed 105 C in order to prevent positive bias because introduced by sulfuric acid carryover to the distillate at the higher temperatures. Some commentators expressed a desire to replace the methods with totally different methods of analysis. They felt they should not be restricted to using only those methods published by the Agency. However, in response to these comments, an equivalent or alternative method may be used after approval by the Administrator according to the provisions of § 60.8(b) of the regulations (as refined in 39 FR 9308).

Fluoride Control

Comments were received which questioned the need for Federal fluoride control because fluoride emissions are localized and ambient fluoride concentrations are very low. As discussed in the preamble to the proposed regulations, fluoride was the only pollutant other than the criteria pollutants specifically named as requiring Federal action in the March 1970 Report of the Secretary of Health, Education and Welfare to the United States (U.S.) Congress. The report concluded that "inorganic fluorides are highly evident and toxic gases which, even in low ambient concentrations, have adverse effects on plants and animals. The United States Senate Committee on Public Works in its report on the Clean Air Amendments of 1970 (Senate Report No. 91-1196, September 17, 1970, page 9) included fluorides on a list of contaminants which have broad national impact and require Federal action.

One commentator questioned EPA's use of section 111 of the Clean Air Act, as amended, as a means of controlling fluorides as pollutants. Again, as was mentioned in the preamble to the proposed regulations, the Preferred Strategies for Fluoride Report by Chemrec (November 1970) concluded that the most appropriate control alternative is through section 111. A copy of this report is available for inspection during normal business hours at the Freedom of Information Center, Environmental Protection Agency, 401 M Street, S.W., Washington, D.C.

Another objection was raised concerning the preamble statement that the phosphate fertilizer industry is a major source of fluoride air pollution. According to the Environmental Protection Agency's Study of Fluoride Emissions

Control" (Contract EHSD 71-14) published in January 1973, the phosphate fertilizer industry ranks near the top of the list of fluoride emitters in the U.S., accounting for nearly 14 percent of the total soluble fluorides emitted every year. The Agency contends that these facts justify naming the phosphate fertilizer industry a major source of fluorides.

Diammonium Phosphate Standard

One commentator contended that the fluoride standard for diammonium phosphate plants could not be met at all under certain extreme conditions (curing periods of high air flow rate through the scrubbing system, high ambient temperatures, and high fluoride content in scrubber liquor). The commentator suggested that the standard would not be met even by sources utilizing best demonstrated control technology. This requirement was refuted for two reasons: (1) The surmised extreme conditions would not occur; and (2) even if the conditions did occur, the performance of the control system would be such as to meet the standard anyway. Thus, the fluoride standard for diammonium phosphate plants was not revised.

Feed Water Standards

The question of the standards for feed water was raised in the comments. The commentator felt that it would have been more logical if the Agency had postponed proposal of the phosphate fertilizer regulations until standards of performance for feed water had also been decided upon. Instead of EPA saying that such feed water standards might be set in the future, EPA recommend feed water standards along with the other fertilizer standards, but due to the complex nature of feed chemistry and a general lack of available information, this simultaneous proposal was not feasible. Rather than delay new source fluoride control regulations possibly for several years, the Agency decided to proceed with standards for the remainder of sources within the industry.

Economic Impact

As was indicated by the comments received, clarification of some of the Agency's statements concerning the economic impact of the standards is necessary. First, the statement that "for three of the six standards there will be no increase in water consumption over that which results from State and local standards" is misleading as written in the preamble to the proposed regulations. The statement should have been modified to read that this conclusion was based on projected construction in the industry through 1980, and was not meant to be applicable past that time. Second, some comments suggested that the cost data in the background document were out of date. Of course the time between the gathering of economic data and the promulgation of regulations may be as long as a year or two because of necessary intermediate steps in the standard setting process. However, the economic data are developed with future industry growth and financial status in mind, and therefore, the analysis should be made at the time of standard proposal. Third, an objection was raised to the statement that "the elasticity in cost between triple superphosphate and diammonium phosphate will only hasten the trend toward production of diammonium phosphate." The commentator felt that EPA should not place itself in a position of regulating fertilizer production. In response, the Agency does not set standards to regulate production. The standards are set to employ the best system of emission reduction considering cost. The standards will hopefully result in the use of a wet scrubber for compliance in each of the five phosphate fertilizer source categories. In this instance, control costs (although considered reasonable for both source categories) are higher for triple superphosphate plants than for diammonium phosphate plants. The reasons for this are that (1) larger gas volumes must be scrubbed in triple superphosphate facilities and (2) triple superphosphate storage facility emissions must also be scrubbed. However, the greater costs can be partially offset in a plant producing both granular triple superphosphate and diammonium phosphate with the same manufacturing facility and some control device. Such a facility can optimize utilization of the control device by operating its phosphoric acid plant at full capacity and producing a product mix that will maximize profits. The information gathered by the Agency indicates that all new facilities designed to manufacture diammonium phosphate will also produce granular triple superphosphate to satisfy demand for direct application materials and exports.

Control of Total Fluorides

Most of the commentators objected to EPA's control of "total fluorides" rather than gaseous and water soluble fluorides. The rationale for deciding to set standards for total fluorides is presented on pages 5 and 6 of volume 1 of the background document. Essentially, the rationale is that some "insoluble" fluoride compounds will slowly dissolve if allowed to remain in the water body for a period of time. The Agency has decided not to closely control the time between capture and filtration of the liquid samples. No change was made to insure a more accurate data base. Additional comments on this subject received concern that the switch to total fluorides would bring phosphate rock operations under the standards. EPA did not intend such operations to be controlled by these regulations and did not include them in the development of affected facilities; however, standards for these operations are currently under development within the Agency.

Monitoring Requirements

Several comments were received with regard to the sections requiring a flow measuring device which is accurate to ± 5 percent over its operating range. The commentators felt that this accuracy could not be met and that the capital and operating costs associated with such a device were not justified in relation to the anticipated utility. First of all, "orifice bells" are common devices in the phosphate fertilizer industry as raw material feeds are routinely measured. EPA felt there would be no economic impact resulting from this requirement because plants would have normally installed weighing or mass meters. Second, contacts with the industry led EPA to believe that the ± 5 percent accuracy requirement would be easily met, and a search of pertinent literature showed that weighing devices with ± 1 percent accuracy are commercially available.

Performance Test Procedures

Finally, some comments specifically addressed § 60.345 (now § 60.344) of the proposed granular triple superphosphate storage facility standards. The first two remarks contended that it is impossible to tell when the storage building is filled to at least 10 percent of the building capacity without requiring an expensive engineering survey, and that it was also impossible to tell how much triple superphosphate is in the building at any time or how much is over 10 days old. EPA's experience has been that plants typically have surveys to determine the amount of triple superphosphate stored, and typically keep good records of the movement of triple superphosphate into and out of storage so that it is possible to make a good estimate of the age and amount of product in bulk. On the basis of data gathered during testing, the Agency disagrees with the above contentions and feels the requirements are reasonable. A third comment stated that § 60.345 (now § 60.344) was too restrictive, could not be met with partially filled storage facilities, and that the 10 percent requirement was not valid or practical to determine. The requirement of § 60.344(a)(3) is that "at least 10 percent of the building capacity contain granular triple superphosphate." This means that for a performance test, an owner or operator could have more than 10 percent of the building filled. In fact it is to his advantage to have more than 10 percent because of the likelihood of decreased emissions (in units of the standard) as calculated by the equation in § 60.344(a). The data obtained by the Agency show that the standard can be met with partially filled buildings. One commentator did not agree with the requirement to have at least five 8-hr maximum production days of fresh granular triple superphosphate in the storage building before a performance test. The commentator felt this section was unreasonable because it dictated production schedules for triple superphosphate. However, this section applies only after the requirements of § 60.344(a)(3) (proposed § 60.345(a)(3)) are met. In addition this requirement is not unreasonable because performance tests are not required of routine control. A performance test is commenced after a facility begins operation; additional performance tests are conducted only when the facility is suspected of violation of the standard of performance.

[illegible]

[illegible]

[illegible]

times or smaller volumes when necessitated by process variables or other factors, may be approved by the Administrator.

(c) The air pollution control system for the affected facility shall be constructed so that volumetric flow rates and total fluoride emissions can be accurately determined by applicable test methods and procedures.

(d) Equivalent P_2O_5 feed shall be determined as follows:

(1) Determine the total mass rate in metric tons/hr of phosphorus-bearing feed during each run using a flow monitoring device meeting the requirements of § 60.334(a).

(2) Calculate the equivalent P_2O_5 feed by multiplying the percentage P_2O_5 content, as measured by the spectrophotometric molybdovanadophosphate method (AOAC Method 9), times the total mass rate of all phosphorus-bearing feed. AOAC Method 9 is published in the Official Methods of Analysis of the Association of Official Analytical Chemists, 11th edition, 1970, pp. 11–13. Other methods may be approved by the Administrator.

(e) For each run, emissions expressed in g/metric ton of equivalent P_2O_5 feed shall be determined using the following equation:

$$E = \frac{(C_s Q_s) \times 10^3}{M_{P_2O_5}}$$

where:

E = emissions of total fluorides in g/metric ton of equivalent P_2O_5 feed,

C_s = concentration of total fluorides in mg/dscm as determined by Method 13A or 13B,

Q_s = volumetric flow rate of the effluent gas stream in dscm/hr as determined by Method 2,

$M_{P_2O_5}$ = equivalent P_2O_5 feed rate, metric tons/hr as determined by § 60.334(d).

Subpart W—Standards of Performance for Florida Phosphate Fertilizer Industry: Triple Superphosphate Plants

§ 60.330 Applicability and designation of affected facility.

The affected facility to which the provisions of this subpart apply is each triple superphosphate plant. For the purpose of this subpart, the plant(s) (facility) includes any combination of: Mixers, curing belts (dens), reactors, granulators, dryers, coolers, screens, mills and facilities which store run-of-pile triple superphosphate.

§ 60.331 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act and in subpart A of this part.

(a) "Triple superphosphate plant" means any facility manufacturing triple superphosphate by reacting phosphate rock with phosphoric acid. A run-of-pile triple superphosphate plant includes curing and storing.

(b) "Run-of-pile triple superphosphate" means any triple superphosphate that has not been processed in a granulator and is composed of particles as that 95 percent by weight of which (when not caked) will pass through a 16 mesh screen.

(c) "Total fluorides" means elemental fluorine and all gaseous fluoride compounds as measured by reference methods specified in § 60.334 or alternative or alternative methods.

(d) "Equivalent P_2O_5 feed" means the quantity of phosphorus, expressed as phosphorus pentoxide, fed to the process.

§ 60.332 Standard for fluorides.

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility any gases which contain total fluorides in excess of 100 g/metric ton of equivalent P_2O_5 feed (0.20 lb/ton).

§ 60.333 Monitoring of operations.

(a) The owner or operator of any triple superphosphate plant subject to the provisions of this subpart shall install, calibrate, maintain, and operate a flow monitoring device which can be used to determine the mass flow of phosphorus-bearing feed material to the process. The flow monitoring device shall have an accuracy of ±5 percent over the operating range.

(b) The owner or operator of any triple superphosphate plant shall maintain a daily record of equivalent P_2O_5 feed by first determining the total mass rate in metric tons/hr of phosphorus-bearing feed using a flow monitoring device meeting the requirements of paragraph (a) of this section and then by procedures according to § 60.334(d)(2).

(c) The owner or operator of any triple superphosphate plant subject to the provisions of this part shall install, calibrate, maintain, and operate a monitoring device which continuously records the production rate (in terms of equivalent P_2O_5 feed) whenever gases from the affected facility are discharged to the atmosphere. The monitoring device shall have an accuracy of ±5 percent over its operating range.

§ 60.334 Test methods and procedures.

(a) Reference methods in Appendix A of this part, except as provided for in § 60.8(b), shall be used to determine compliance with the standards prescribed in § 60.332 as follows:

(1) Method 13A or 13B for the concentration of total fluorides and for associated moisture content.

(2) Method 1 for sample and velocity traverses.

(3) Method 2 for velocity and volumetric flow rate.

(4) Method 3 for gas analysis.

(5) For Method 13A or 13B, the sampling time for each run shall be at least 60 minutes and the minimum sample volume shall be at least 1.70 dscm (60 dscf) except that shorter sampling times or smaller volumes, when necessitated by process variables or other factors, may be approved by the Administrator.

(b) The air pollution control system for the affected facility shall be constructed so that volumetric flow rates and total fluoride emissions can be accurately determined by applicable test methods and procedures.

(c) Equivalent P_2O_5 feed shall be determined as follows:

(1) Determine the total mass rate in metric tons/hr of phosphorus-bearing feed during each run using a flow monitoring device meeting the requirements of § 60.333(a).

(2) Calculate the equivalent P_2O_5 feed by multiplying the percentage P_2O_5 content, as measured by the spectrophotometric molybdovanadophosphate method (AOAC Method 9), times the total mass rate of all phosphorus-bearing feed. AOAC Method 9 is published in the Official Methods of Analysis of the Association of Official Analytical Chemists, 11th edition, 1970, pp. 11–13. Other methods may be approved by the Administrator.

(d) For each run, emissions expressed in g/metric ton of equivalent P_2O_5 feed shall be determined using the following equation:

$$E = \frac{(C_s Q_s) \times 10^3}{M_{P_2O_5}}$$

where:

E = emissions of total fluorides in g/metric ton of equivalent P_2O_5 feed,

C_s = concentration of total fluorides in mg/dscm as determined by Method 13A or 13B,

Q_s = volumetric flow rate of the effluent gas stream in dscm/hr as determined by Method 2,

$M_{P_2O_5}$ = equivalent P_2O_5 feed rate, metric tons/hr as determined by § 60.334(d).

Subpart X—Standards of Performance for Florida Phosphate Fertilizer Industry: Triple Superphosphate Plants

§ 60.330 Applicability and designation of affected facility.

The affected facility to which the provisions of this subpart apply is each triple superphosphate plant. For the purpose of this subpart, the plant(s) (facility) includes any combination of: Mixers, curing belts (dens), reactors, granulators, dryers, coolers, screens, mills and facilities which store run-of-pile triple superphosphate.

§ 60.331 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act and in subpart A of this part.

(a) "Triple superphosphate plant" means any facility manufacturing triple superphosphate by reacting phosphate rock with phosphoric acid. A run-of-pile triple superphosphate plant includes curing and storing.

(b) "Run-of-pile triple superphosphate" means any triple superphosphate that has not been processed in a granulator and is composed of particles as that 95 percent by weight of which (when not caked) will pass through a 16 mesh screen.

(c) "Total fluorides" means elemental fluorine and all gaseous fluoride compounds as measured by reference methods specified in § 60.334 or alternative methods.

(d) "Equivalent P_2O_5 feed" means the quantity of phosphorus, expressed as phosphorus pentoxide, fed to the process.

§ 60.332 Standard for fluorides.

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility any gases which contain total fluorides in excess of 100 g/metric ton of equivalent P_2O_5 feed (0.20 lb/ton).

§ 60.333 Monitoring of operations.

(a) The owner or operator of any triple superphosphate plant subject to the provisions of this subpart shall install, calibrate, maintain, and operate a flow monitoring device which can be used to determine the mass flow of phosphorus-bearing feed material to the process. The flow monitoring device shall have an accuracy of ±5 percent over the operating range.

(b) The owner or operator of any triple superphosphate plant shall maintain a daily record of equivalent P_2O_5 feed by first determining the total mass rate in metric tons/hr of phosphorus-bearing feed using a flow monitoring device meeting the requirements of paragraph (a) of this section and then by procedures according to § 60.334(d)(2).

(c) The owner or operator of any triple superphosphate plant subject to the provisions of this part shall install, calibrate, maintain, and operate a monitoring device which continuously records the production rate (in terms of equivalent P_2O_5 feed) whenever gases from the affected facility are discharged to the atmosphere. The monitoring device shall have an accuracy of ±5 percent over its operating range.

§ 60.334 Test methods and procedures.

(a) Reference methods in Appendix A of this part, except as provided for in § 60.8(b), shall be used to determine compliance with the standards prescribed in § 60.332 as follows:

(1) Method 13A or 13B for the concentration of total fluorides and for associated moisture content.

(2) Method 1 for sample and velocity traverses.

(3) Method 2 for velocity and volumetric flow rate.

(4) Method 3 for gas analysis.

(5) For Method 13A or 13B, the sampling time for each run shall be at least 60 minutes and the minimum sample volume shall be at least 1.70 dscm (60 dscf) except that shorter sampling times or smaller volumes, when necessitated by process variables or other factors, may be approved by the Administrator.

(b) The air pollution control system for the affected facility shall be constructed so that volumetric flow rates

[illegible]

Place the crucible in a cold muffle furnace and gradually (to prevent smoking) increase the temperature to 600°C. Ignite at this temperature for 15 minutes. Remove the crucible from the furnace and allow it to cool.

5.2.8 Add approximately 5 g of prepared reagent to the crucible and heat to fuse the contents. Pour the melt into the platinum dish and heat the crucible for 10 minutes at 600°C.

Remove the crucible from the furnace and cool to ambient temperature. Using a small amount of warm distilled water, transfer the contents of the crucible to the beaker containing the filtrate from container No. 1 (5.2.1). To ensure complete sample removal, rinse finally with two 20 ml portions of 20 percent (V/V) sulfuric acid and carefully add to the beaker. Stir well and transfer a portion of the solution to a 50 ml colorimetric flask. Dilute to volume with deionized water and mix thoroughly. Allow any undissolved solids to settle.

5.2.9 Calibration No. 2. Assign the spectrophotometer No. 2 designation to the spectrophotometer used.

5.2.10 Adjustment of acid-water ratio in distillation flask. (Neither a protective shield nor personnel protection is required when carrying out this procedure.) Place 300 ml of distilled water in the distilling flask and add 200 ml of concentrated H_2SO_4. Caution: Observe standard precautions when mixing the acid by, for example, adding the acid to the water with constant agitation. Add several glass beads and several small pieces of broken glass to the flask and assemble the apparatus as shown in Figure 13A-2. Heat the flask until it reaches a temperature of 175°C to adjust the acid-water ratio for subsequent distillations. Discard the distillate.

5.2.11 Distillation. Heat the contents of the distillation flask to below 80°C. Pipette an aliquot of sample containing less than 0.5 mg F (by one of the procedures in Section 5.1) into the distilling flask and add enough distilled water to make a total volume of 300 ml prior to the addition of the sample. Add 50 ml of concentrated H_2SO_4. Caution: Observe standard precautions when mixing the acid by, for example, adding the acid to the water with constant agitation. Add several glass beads

$$V_{std} = V_m \frac{P_{std}}{P_m} \left[\frac{T_{std} + \Delta H}{T_m + \Delta H} \right] - K V_w \frac{P_{std} + \Delta H/13.6}{P_m}$$

equation 13A-1

where:
K = 0.4854 in mm Hg for metric units
= 17.64 °R/in. Hg for English units.
V_w = Volume of water vapor.

$$V_{std} = V_m \frac{P_m}{M_m} \frac{M T_{std}}{P_{std}} - K V_w$$

equation 13A-2

where:
M = 0.0454 in mol for metric units
= 0.0418 in lb-mol for English units.
B_{ws} = Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{w(std)} + V_{m(std)}}$$

equation 13A-3

If the liquid droplets are present in the gas stream, assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

C_s = Concentration.

7.6.1 Calculate the amount of fluoride in the sample according to Equation 13A-4.

$$F_s = K \frac{V_s V_{soln}}{A_1 A_2} (ug F)$$

equation 13A-4

where:
K = 10^3 mg/ug.
C_{sa} = Concentration of fluoride in stock (25.0) determine the concentration of fluoride in the stock gas according to Equation 13A-5.

$$C_s = K \frac{F_s}{V_{m(std)}}$$

equation 13A-5

where:
K = 35.31 ft^3/m^3.
7.7 Isokinetic variation.
7.7.1 Calculations from raw data.

$$I = \frac{100 T_s [K V_{lc} + (V_m/T_m)(P_{bar} + \Delta H/13.6)]}{60 \theta v_s P_s A_n}$$

equation 13A-6

where:
K = 0.00346 cu m/ug-mol-°K for metric units.
= 0.00267 cu ft-in. Hg/ug-mol-°R for English units.
v_s = Calculations from intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{v_s \theta A_n P_s 60 (1 - B_{ws})} = K \frac{T_s V_{soln}}{P_s v_s A_n \theta (1 - B_{ws})}$$

equation 13A-7

where:
K = 4.323 for metric units.
= 0.0945 for English units.

7.8 Acceptable results. If 90 percent ≤ I ≤ 110 percent, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may option to accept the results. Use reference 7.4 to make judgments. Otherwise, reject the results and repeat the test.

10. References.

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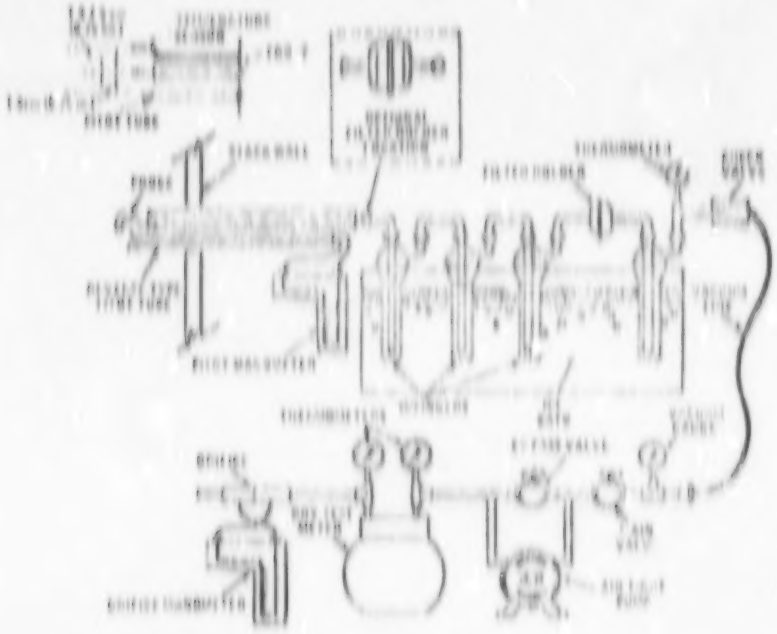

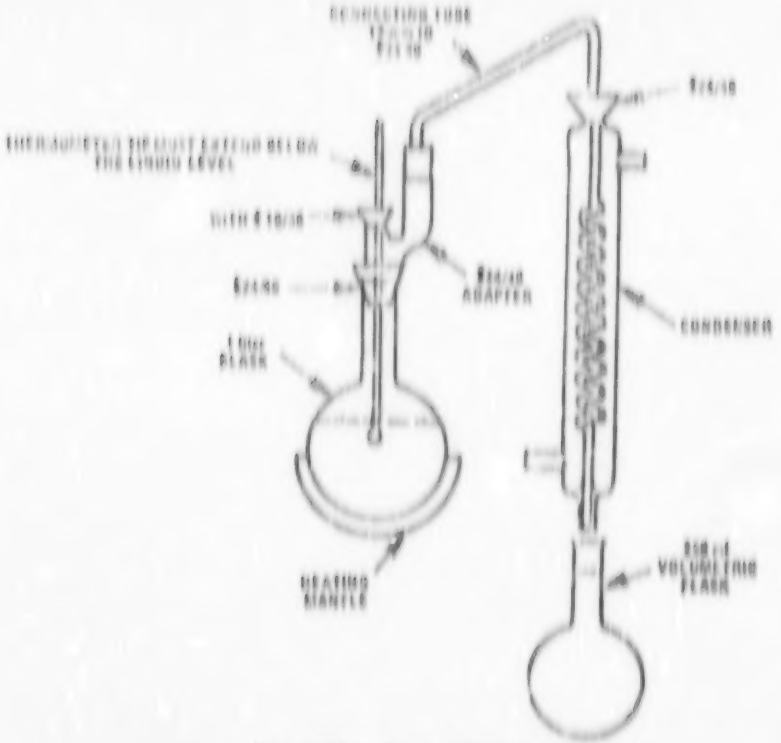

Figure 13A-7. Fluoride Distillation Apparatus

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